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TRACES OF HEAVY METALS IN WATER REMOVAL PROCESSES AND MONITORING

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REMOVAL PROCESSES AND MONITORING

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TRACES OF HEAVY METALS IN WATER
REMOVAL PROCESSES AND MONITORING

Edited by J. E. Sabadell

Proceedings of a Symposium conducted by the
Center for Environmental Studies and the
Water Resources Program

Princeton University

in cooperation with the

United States Environmental Protection Agency - Region II

and the

American Institute of Chemical Engineers
Environmental Division

November 15-16, 1973

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PREFACE

It is by now generally accepted that the practice of disposing of our industrial, domestic and agricultural wastes in air, soil and waters is taxing our environment beyond capacity, and in some instances with catastrophic consequences.

From a host of solutes present in our waters heavy metal traces in their ionic state belong to the category of man-made pollutants that can be highly toxic to humans, animals and plants by accumulating in the organism affecting bones, skin, organs, nervous and other systems, producing chronic diseases and even death, as it occurred in Minamata between 1953-1960, in Niigata in 1965, in Iraq in 1960 and in Pakistan in 1961. The number of problems, in the water resources field, that need to be solved are enormous. In this symposium, organized by the Center for Environmental Studies at Princeton University, only two questions were addressed: 1) Which processes can efficiently remove these traces of heavy metals? and 2) how can these traces, sometimes in the part per billion level, be more accurately measured? To partially answer these questions, a group of scientists and engineers were invited to present their findings on these subjects. With the sponsorship of the United States Environmental Protection Agency - Region II, the American Institute of Chemical Engineers, and the Water Resources Program of Princeton University, the program was presented November 15-16, 1973 at the School of Engineering/Applied Science of Princeton University.

J. Eleanora Sabadell
Symposium Director

OVERVIEW OF DRINKING WATER QUALITY CONTROL AT THE FEDERAL LEVEL

Robert W. Mason, Chief, Research & Development Branch
Region II, Environmental Protection Agency

The Environmental Protection Agency is primarily a regulatory agency. All of its programs, and this includes the research and development program, are structured so as to enable the Agency to carry out its regulatory function of protecting the environment and abating and avoiding pollution. Following are the six major emphases of the R&D program:

SLIDE 1

1. The development of appropriate science and technology for setting and enforcing pollution control standards.
2. Development of the full understanding of the environmental impact of that which we are mandated to control.
3. The knowledge of what it "costs" to meet environmental quality standards.
4. Knowledge of the "costs" of not meeting environmental standards (i.e., the benefits to be derived from meeting them).
5. Monitoring to meet environmental goals and
6. Establishment of the means of forecasting the long range effects.

Evaluating the costs of meeting and not meeting standards means putting a dollar value not only on the labor required to institute, say, an industrial process improvement but also on the lost (or gained) human health, enjoyment and other aspects of the quality of life.

I could spend a great deal more time discussing what is implied in these six major areas for they contain implicitly the entire EPA Research and Development program. This is both the in-house and extramural program which is administered by Washington Headquarters and the four National Environmental Research Centers at Research Triangle Park, North Carolina; Cincinnati, Ohio; Las Vegas, Nevada; and Corvallis, Oregon. Each one of these NERCs, as they are called, has a theme for its research. RTP is Human Health Effects, Cincinnati is Technology and Process Development, Las Vegas is Research Monitoring, and Corvallis is Ecology, or the effects of pollutants on the environment. All the work on drinking water quality and on health effects related to drinking water is carried out at the Cincinnati Laboratory. Work on recreational water is carried out at Cincinnati and at the Narragansett Laboratory because of the latter's location near marine beaches.

The Water Supply Research Program is presently being carried out under the authority of the Public Health Service Act (Public Law 410, 78th Congress). The Reorganization Plan of 1970 transferred the function of the Water Supply Program from the Department of Health, Education and Welfare to the newly established Environmental Protection Agency. Under the Public Health Service Act and the Reorganization Plan the Environmental Protection Agency is responsible for the certification of water supply for interstate carrier use and also has authority to conduct and encourage research on water purification. The Safe Drinking Water Act is presently awaiting passage by Congress. A little later on I'll discuss some of the provisions of this new Act which broaden the authority of EPA.

Please let me digress for a moment. Some of you are college professors and are undoubtedly interested in government gold. As you have probably gathered, after having received rejection notices from one agency or another, on some of your proposals, there is very little of it around. However, if you have a proposal which is deemed "relevant to our research program" and responsive to a high priority research need, there is a chance for funding. If you are in Region II, that is in New York, New Jersey, the Virgin Islands or Puerto Rico, you may submit these proposals in abbreviated form as "pre-proposals" directly to me and I will obtain an evaluation of their relevancy and responsiveness to our needs from our specialists. My office is in New York City at 26 Federal Plaza.

Now let us turn to Nora Sabadell's program, "Traces of Heavy Metals in Water; Removal Processes and Monitoring". SLIDE 2 shows the Public Health Service 1962 standards which are presently used by EPA for interstate carriers. I've only listed heavy metals here.

SLIDE 2

	1962 Concentration mg/l	Proposed Concentration mg/l
Arsenic	0.05	0.1
Copper	1.0	1.0
Iron	0.3	0.3
Manganese	0.05	0.05
Zinc	5	5
Mercury	-	0.002
Barium	1	1
Cadmium	0.01	0.01
Lead	0.05	0.05
Selenium	0.01	0.01
Silver	0.05	0.05
Chromium	0.05	0.05

The proposed revisions, which have not yet been approved, are shown in the second column. You'll notice the only difference is that arsenic is raised to 0.1 mg/l and a value for mercury, which was lacking in the original 1962 figures, is included. I am sure you will agree that publishing a revised list of heavy metal standards for drinking water will not end the matter. The actions and interactions of trace metals in the animal organism are very complex. We know a lot about lead, but the lead poisoning problem is still with us as higher and higher levels are being found in human tissues. Too little can cause problems as well as too much. Cadmium has been linked to various ailments although the only proven pathology from too much Cadmium ingestion appears to be the "itai-itai" or "ouch-ouch" disease in Japan. Manganese needs to be studied further as deficiencies can cause poor growth, skeletal abnormalities and sterility, at least in male guinea pigs. Chromium is important in small amounts but little is known as to how it works, and so on. Work will obviously have to be continued in the field of health effects of trace metals. In fact the new legislation provides for review of the standards every three years.

The present EPA water supply research program is carried out under two broad headings: (1) Water Supply Health Effects and (2) Water Supply Control Technology. SLIDES 3 and 4 show the detailed breakdown of expenditures in the program.

SLIDE 3

WATER SUPPLY HEALTH EFFECTS RESEARCH

	1973	1974
Establish Health Criteria for Unknown Organic Contaminants of Drinking Water	226,000	
Establish Health Criteria for Inorganic Chemical Constituents of Drinking Water	285,000	
Investigate Problems of Infectious Water Born Disease	430,000	
*Review Safety of Products Used in Water Treatment, Storage and Distribution and Unique Water Sources	60,000	
Develop Criteria to Establish and Support Safe Recreational Water Quality Standards	260,000	
TOTAL	$1,261,000	$1,568,000
EXTRAMURAL	165,000	379,000

*Unique Water Sources refer to waste water reuse.

SLIDE 4

WATER SUPPLY CONTROL TECHNOLOGY

	1973	1974
Evaluation and Improvement of Treatment Processes for the Removal of Trace Organics and Taste and Odor	$ 109,000	
Evaluation and Improvement of Treatment Processes for the Removal of Turbidity and Specific Particles	16,000	
Evaluation and Improvement of Treatment Processes for Reduction of Trace Metals and Nitrate Concentrations	82,000	
Evaluation and Improvement of Methods for Killing or Inactivating Micro-organisms in Drinking Water	86,000	
Evaluation and Prevention of Chemical Quality Deterioration During Distribution of Drinking Water	113,000	
The Study of the Behavior and Control of Contaminants and Additives in Drinking Water Sources During Storage	65,000	
Evaluation and Control of Bacterial Quality Deterioration of Potable Water in Distribution Systems and Bottled Water Supplies	112,000	
TOTAL	$ 583,000	$ 587,000
EXTRAMURAL	60,000	130,000

Now let us turn briefly to the implications of the new drinking water bill. This is entitled the Safe Drinking Water Act of 1973 (Senate 433 and HR 5368). Under these new bills prime responsibility for maintaining the quality of drinking water will remain with state and local governments. But the Federal Government will exercise a new responsibility to set standards and provide assistance in order to protect public water supplies (not just supplies to interstate carriers) from contamination. Among other things the proposed legislation provides that EPA establish minimum federal drinking water standards prescribing maximum limits for contaminants. EPA is also to set standards for the operation and maintenance of drinking water systems as well as standards for monitoring, site selection, and construction of public water systems to assure safe dependable drinking water. A few words on the definition of the term public water system: aside from water used in interstate carriers on which there is no size limitations, the term means any system which provides drinking water to 10 or more premises not owned or controlled by the supplier of water or to 40 or more individuals, any system which provides drinking water to carriers or establishments serving travellers in interstate commerce, or any other system which provides drinking water. if the Administrator of EPA determines that such a system may pose an unreasonable threat to public health. The legislation then goes on to say that EPA is to establish recommended standards to assure esthetically adequate drinking water, while the States can, of course, establish standards which are more stringent. The States will be primarily responsible for enforcing the standards with Federal enforcement if the States fail to act, or in case of imminent hazard, EPA will conduct and promote research, technical assistance, and training of personnel for water supply occupations. EPA will conduct a rural water survey within 2 years of enactment of the new bill. EPA will make grants for special studies and demonstration projects with respect to water supply technology. EPA will make grants to States to defray the cost of the State program. Citizens will be authorized to bring injunctive suits to violators of primary drinking water standards and against the Administrator for failing to perform mandatory duties. Of particular importance to most of us is the section in the proposed legislation which contains a specific authorization for research, technical assistance, information and the training of personnel for the current fiscal year as well as for the next two fiscal years. The amount authorized shall not exceed 14 million dollars for Fiscal Year 1974. $14 million is about seven times our present rate of expenditure. We don't expect $14 million to be actually appropriated but we expect a sizeable increase over present expenditures if the legislation is passed. There is also a $2 million authorization in 1974 for special studies in demonstration project grants intended to support the demonstration of new technology and not for use in the construction and operation of any facility unless that facility demonstrates new technology. There are other provisions but I think I have covered the thrust of the new legislation so far as research is concerned.

To epitomize the new act, EPA will be given authority to set national drinking water standards and to carry out research on the identification and health effects of drinking water contaminants, on water treatment technology and health effects of water reuse.

In summary, I have told you very briefly about the general research objectives of the Environmental Protection Agency and the allocation of funds to drinking water research activities. I have pointed out that EPA's responsibility for drinking water quality is at present limited to certification of water quality on interstate carriers but that it will probably be broadened by the enactment of the so-called Safe Drinking Water Act of 1973.

A few words about future research - we are moving toward water reuse. The American Water Works Association believes that "the full potential of reclaimed water as a resource should be exploited as rapidly as specific knowledge and technology will allow". The research tasks which need to be carried out, which are of direct interest to this conference, are:

(1) Determine the concentrations of harmful contaminants in water and the degree to which they can be removed.

(2) Define the testing procedures, analytical methodology, allowable limits, and monitoring systems that should be employed with respect to the use of reclaimed waste water for public water supply purposes.

TRACE HEAVY METAL REMOVAL BY ION EXCHANGE

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Introduction

The first successful ion exchange process was water softening, developed about sixty years after the process discovery in 1848. Today, the major application of the ion exchangers is still water softening for household, municipal and industrial uses. The next major application of ion exchange is deionization which has replaced for many requirements evaporation and distillation.

It can be said that the driving force for obtaining purer and purer water was from the power utilities which for greater efficiency and productivity introduced boilers operating at very high temperatures and pressures where solids in the steam can deposit on the turbines and walls of the boilers, resulting in heavy maintenance cost and shutdowns. This drive resulted in the search for better ion exchangers to meet the needs of the industry.

The hydrometallurgical market appeared at the end of the war with the rise of the nuclear industry. Recovery of uranium, treating nuclear plant wastes and separation of nuclides are now basic ion exchange processes. Other common industrial uses of ion exchanger for metal ion removal and recovery are copper and zinc recovery in rayon production, chromates in blow off from cooling waters, gold, copper, nickel, zinc, chromium, etc., from plating rinses waters, rare earth separation, etc. Until recently the economics of the value of the recovered metal was the dominant factor in plant construction.

At present, government regulations for effluent discharges of heavy metal ions into streams are becoming stricter with limits set for many in less than ppm quantities. This may stimulate the development of new ion exchangers or complexing resins specific for given metallic entities because of the new commercial market that may open. Till now most of the specific ion exchangers have been prepared in academic laboratories or through government contracts for specific ions, e.g., ammonia, nitrate, boron, etc. What is needed today is a systematic approach for preparing and evaluating specific ion exchangers and chelate resins for trace metal removal

*Former address Sybron Corporation, West Orange, N.J. 07052 on a practical and economic basis. Most of the present ion exchangers operate on a selective affinity so many innocuous ions are also removed at the same time and therefore the volume of waste regenerant is high and the metal ion which may have value is obtained as a mixture requiring further purification steps.

Just as the research in the Manhattan project produced the base for ion exchange applications to the nuclear field, a similar unified approach is essential to the progress of metal ion removal rather than the present procedure of waiting of chance contract proposals.

Another important outcome of the polymeric organic ion exchangers, which will grow in importance is the development of synthetic polymeric adsorbents which can remove metal oxides and organics if polar groups are present and organic pollutants if no polar groups are present on the adsorbent.

Ion Exchange--Basic Reactions and Selectivity

The basic reactions of the available commercial resins are similar to the behavior of strong and weak electrolytes depending on the functional group present in the resin. Thus a strongly acidic ion exchanger containing a sulfonic group in the hydrogen form will react with sodium chloride according to equations 1 and 2.

$$RSO_3H_r + Na_s^+ \rightleftharpoons RSO_3\,Na_r + H_s^+ \qquad (1)$$

$$2RSO_3\,Na_r + Ca_s^{++} \rightleftharpoons (RSO_3)_2\,Ca_r + 2Na_s^+ \qquad (2)$$

Where R is the resin matrix, r on resin, s in solution. The reactions are reversible the direction depending on the concentrations involved.

A weakly acidic ion exchanger containing a carboxylic group in the hydrogen form will not react with a neutral salt as the affinity for the hydrogen is greater than for the sodium, i.e.

$$RCO_2H + NaCl \not\rightleftharpoons RCO_2\,Na + HCl \qquad (3)$$

However, if the anion of the salt forms a weaker acid than the acidic group on the resin exchange will take (cf. eq. 4) similarly the salt form of the exchanger will undergo exchange with neutral salts depending on the selectivity of the resin for the specific ion in solution (cf. eq. 5). The selectivity of the carboxylic resin for multivalent ions is so high that frequently the resin is used to reduce the concentration of these ions below the solubility product of the most insoluble salts of the ion. Also, it must be recognized that H_2CO_3 in water will cause the exchanger to become in the H form due to the high selectivity for the H ion.

$$RCO_2H + NaHCO_3 \longrightarrow RCO_2N_a + H_2CO_3 \uparrow \qquad (4)$$

$$2RCO_2Na + Ca^{++} \rightleftharpoons (RCO_2)_2Ca + 2Na^+ \qquad (5)$$

The equilibrium theory applied to equation 1 can aid in predicting the quantity an ion will be associated with the resin when in equilibrium with a given solution of the ion. In the simplest manner the mass action equilibrium constant can be equated to the selectivity coefficient. The mass action relation of equation (1) can be expressed

$$K = \frac{Na_r^+ \times H_s^+}{H_r^+ \times Na_s^+}$$

or

$$K = \frac{Na_r^+}{Hr^+} \Big/ \frac{Na_s^+}{Hs^+}$$

As K has not been found to be a constant as it varies with the ionic concentration and loading on the resin and as the knowledge of the activity coefficients of the ions in the resin is limited, the equilibrium constant is considered as a selectivity coefficient rather than an equilibrium constant. Table I shows the variation of the so called constant with mole fraction of the ions in solution.

TABLE I

Observed selectivity coefficients of an 8% cross linked sulfonated polystyrene exchanger (Data by Myers Boyd, et al, cf. Helfferic reference)

Ionic Composition	Na^+-Li^+ exchange	Na^+-H^+ exchange
0% Na^+		
0	1.72	1.38
50	1.80	1.52
100	1.89	1.20

As the ion exchange resins have fixed pores (macroreticular resins) or form pores on swelling in water (gel type resins), ions or complexes larger than the pores are excluded by sieve action. This exclusion depends in the gel type resins on the cross linking of the matrix. Table II shows the variation of capacity of polystyrene type cation exchangers for a large organic cation.

TABLE II

Relative capacities (%) of polystyrene cation exchangers for Dinbenzyl dimethyl ammonium ion.

%DVB	2	5	10	15
Relative capacity %	100	94	43	15

The selectivity coefficients for various metal ions will be given later.

Kinetics of Ion Exchange

The rate of exchange is favored by the following conditions:

1. The smaller the particle size
2. Efficient mixing of the exchanger with the solution (batch process)
3. High temperature
4. High concentration of solution
5. The smaller the ion size
6. The more porous the exchanger
7. Nature of the ionic group
   Rate lower for weak exchangers
8. High capacity of the exchanger

Parameters in Efficient Column Operation

Usually these will be found to be:

1. High affinity of the exchanger for an ion
2. Elevated temperatures
3. High capacity of the exchanger (volume)
4. The smaller the particle size
5. The more uniform the particles of resin
6. High porosity
7. Low flow rate
8. The lower the concentration of the ion
9. The higher the column length.

Methods of Operation

1. Single bed or beds
2. Dual or stratified beds
3. Mixed beds

----

1. Batch
2. Cyclical
3. Countercurrent
4. Continuous counter current

Normal steps of a cycle

Regeneration
Rinse
Run or Exhaustion
Backwash

In mixed beds

Regeneration
Rinse
Air Mix
Rinse
Run
Separate by backwash

The Commercial Ion Exchangers

A. Forms

- The commercial ion exchangers are available in forms of

Particles, granular or beads (Diamond Shamrock, Dow, Ionac, Rohm & Haas)
Membranes (Ionac, Ionics, DuPont)
Paper-cellulosic (Whatman-Reeve Angel)
Fibers and Fabrics (Carborundum)
Foamed Resin (Scott Paper)
Tubes (Various labs)

B. Physical Structure

The standard commercial addition polymeric resins are prepared in three porosity structures.

STRUCTURE OF TYPICAL ION EXCHANGE RESINS

Gel	Polymer bead is prepared as a suspension in water. Resulting structure possesses varying degree of crosslinking; thus, swelling pores of varying sizes are formed. The fine pores that are formed tend to foul quickly.
Fixed pore (macroreticular, macroporous)	Polymer is prepared in presence of solvent in which the monomer but not polymer is soluble, resulting in the formation of discrete pores in the bead on phase separation. The pores are larger than molecular size, and to strenthen the resin structure a greater degree of crosslinking is employed than in gel-type resins.
Isoporous	Final resin possesses a more uniform pore structure than gel-type resin. Uniform pore size is achieved through use of a temporary crosslinking agent that is uniformly distributed throughout the resin and which is destroyed in subsequent processing of the resin.

C. Variations in cross linking, particle sizes and color.

Standard Crosslinking - Crosslinking in polymers 8 to 8.5 molar percent with major portion of the bead sizes in the -20 to +35 mesh.

Lower Crosslinking Products - Between 5 and 7% used in some operations where sturdiness not required; also for throwaway uses.

Higher Crosslinked Products - Used for higher temperatures in the presence of low quantities of oxidizing compounds, or in mixed beds of ultrapure water systems.

Coarse Products - Are the same as the above except the quantity of fine particles are reduced to a minimum; these resins are used for high flow systems, e.g. condensate demineralization.

Partially Dry Resins - The standard resins have a water retention about 46 to 47%. These can be dried to about 25% moisture without cracking or breaking of the beads when placed in water. This makes possible cheaper freight rates and also better storage under freezing conditions.

Stratifying Resins - For better separation of beds in layered systems, the resins involved are varied in size, the lighter one (or top) being finer than the one resting on the botton.

Light Colored Resins - When dyes are introduced as indicators light colored resins are required; some prefer the light colored resins for aesthetic reasons.

Trap Type - Anion exchange resins which are not readily fouled due to their large pores. The capacity if much lower than the standard resins.

Fine beads - In the -50 to 200 mesh.

Micro Fine Beads - In the micron size used in chromatography.

Powdered Resins - -200 mesh for particulate and ion removal.

D. Functional Groups

The present commercial ion exchangers contain the following functional groups.

Cation Exchangers

$-SO_3H$
$-CO_2H$
$-PO_3H_2$
$-PO_2H$
$-SH$
$-OH$

Anion Exchangers

$-NH_2$, $=NH$, $\equiv N$
≣N^+ Cl - Quaternary N
≣N^+ Cl - Pyridinium (Ionac)
$\equiv S^+$ Cl - Sulfonium (Dow)
≣P^+ Cl - Phosphonium

The last three are specialties of certain labs.

Mixed group exchangers containing $-SO_3H$ and $-CO_2H$ groups or both cation and anion exchange groups are also available.

The chelates and specific ion exchange resins will be discussed later.

Also available from various suppliers are:

1. Inorganic exchangers (BioRad, Ionac, Union Carbide)
2. Electron and Redox Ion Exchangers (Diamond-Shamrock)
3. Liquid Ion Exchangers (Dow, General Mills, Rohm & Haas, etc.)
4. Retardation resin (Dow)
5. Organic adsorbents (Rohm & Haas)

E. Types of Polymer Matrices

1. Natural polymeric materials
2. Modified natural polymeric products
3. Synthetic polymers - condensation
4. Synthetic polymers - addition

F. Grades of Ion Exchangers Depending on Use

1. Analytical
2. Chromatographic
3. Food
4. Indicator
5. Nuclear
6. Pharmaceutical
7. Household Use
8. Industrial
9. Uranium Recovery

Processes Used in Combination with Ion Exchange.

Due to the presence various entities in water or waste water and the limitation of the ion exchange process, other treatment processes are frequently used in conjunction with it. Some of these processes are:

1. Filtration
2. Coagulation
3. Adsorption
4. Precipitation
5. Reverse Osmosis
6. Electrodialysis
7. Degasification
8. Disinfection
9. Distillation or evaporation
10. Oxidation or reduction

Usually the combination will be determined by

1. Required purity of the water
2. The concentration and type of contaminants in the water
3. The economics involved

Also, certain entities found in water foul the ion exchangers; removal of these are often a necessity. Therefore, pretreatment is carried out similar to other desalination processes.

Interfering Substances.

Natural (e.g. humates) and man made compounds (e.g. sequestering agents) can complex metal ions so that removal by ion exchange becomes difficult or not at all. Cyanides and humates can be destroyed by chlorination.

In determining the heavy metals, one must recognize the contribution made by materials of construction. Ultrapure water stored in the following list of materials were found to contain ions.

Titanium - very low in metal ions
Tin - Ca, Pb & Zn in ppm quantities
Glass - Boron, 20 ppb
Aluminum - Aluminum, 15 ppb
Stainless Steel 304 - Iron, 2 - 18 ppb
Stainless Steel 316 - low in metals

Adsorption of metals on glass and plastics must be guarded against. Similarly, distilled and deionized water made up for reagents may contribute errors due to trace metals present in industrial resins. The maximum of heavy metals in deionized water is in the 10^{-5} ppm.

Spectrographic analysis of freshly prepared deionized water by mixed beds showed the following concentrations in ppb quantities.

Al		0.1
Sb	$<$	0.5
Be	$<$	0.005
Bi	$<$	0.1
B		3
Cd	$<$	0.1
Ca		1
Cr	$<$	0.1
Co	$<$	0.1
Cu		0.2
Ga	$<$	0.2
Ge	$<$	0.5
Fe		0.2
Pb		0.1
Mg		0.3
Mn		0.05
Hg	$<$	1
Mo	$<$	0.1
Ni	$<$	0.1
Nb	$<$	0.1
Si	$<$	0.5
Ag		0.01
Na		1
Sn	$<$	0.1
Ti	$<$	0.1
V	$<$	0.1
Zn	$<$	0.1
Zr	$<$	0.1

Forms of Heavy Metal Components in Water

The heavy metals are found in water in various forms, (1) as particulates or colloids as a result of

- A. From natural sources
- B. Reactions of the ions with other entities in the water. (e.g., Fe_2O_3 formation through the reaction of Fe^{++} with oxygen).
- C. From pollution.
- D. From treatment chemicals (e.g., Al_2O_3 or Fe_2O_3 after coagulation)
- E. From materials of construction (e.g. corrosion or erosion products)

(2) As ions both cations and anions, mostly from natural sources (e.g. $As_2O_3^{=}$) or pollution ($CrO_4^{=}$)

(3) As complexes with natural organics, or bioorganics, and organic pollutants.

Ion exchangers play a role in the removal of each with certain limitations.

Table III is a list of all the metallic ions to which ion exchangers have been applied in concentration, separation, or purification. Many of these industrial processes are in existence while others have only been utilized in analytical work. The two books on analytical procedures utilizing ion exchangers should be consulted for their references and for techniques used.

Table IV gives a list of the metallic ions often found in water for which ion exchange processes are in use or can be utilized if need arises.

In this paper the various ion exchange techniques applied to removal of the various forms of the heavy metals will be discussed.

Ion Exchangers as Filters

Ion exchange beds do act as filters for particulates within certain limits. However, it is not desirable as physical blockage of pores of the resin can take place with a resultant drop in capacity for ion removal and in quality of effluent and an increase in head loss. Also, colloidal organic or bioorganics with polar groups can react

TABLE III

Ion Exchange Utilized in Conjunction with Metal Ions

1. Actinium and actinides
2. Alkali metals
3. Aluminum
4. Antimony
5. Arsenic
6. Americium
7. Barium
8. Beryllium
9. Bismuth
10. Boron
11. Cadmium
12. Calcium
13. Californium
14. Cerium
15. Cesium
16. Chromium
17. Cobalt
18. Columbium
19. Copper
20. Curium
21. Dysprosium
22. Erbium
23. Europium
24. Ferric ion
25. Ferrous ion
26. Godolinium
27. Gallium
28. Germanium
29. Gold
30. Hafnium
31. Holmium
32. Indium
33. Lanthanum and lanthanides
34. Lead
35. Lithium
36. Lutetium
37. Magnesium
38. Manganese
39. Mercury
40. Molybdenum
41. Neodymum
42. Nickel
43. Niobium
44. Osmium
45. Palladium
46. Platinum
47. Plutonium
48. Polonium
49. Potassium
50. Praseodymium
51. Promethium
52. Radium

32a. Iridium

53. Rare earths
54. Rhenium
55. Rhodium
56. Rubidium
57. Ruthenium
58. Samarium
59. Scandium
60. Selenium
61. Silver
62. Sodium
63. Strontium
64. Tantalum
65. Technetium
66. Tellurium
67. Terbium
68. Thallium
69. Thorium
70. Thulium
71. Tin
72. Titanium
73. Tungsten
74. Uranium
75. Vanadium
76. Yttrium
77. Zinc
78. Zirconium

TABLE IV

Trace Heavy Metals Removed from Water and Waste Waters

1. Aluminum
2. Arsenic
3. Barium
4. Boron
5. Cadmium
6. Chromium
7. Cobalt
8. Copper
9. Germanium
10. Gold
11. Iron
12. Lead
13. Manganese
14. Mercury
15. Nickel
16. Radioactive nuclides
17. Selenium
18. Silver
19. Uranium
20. Zinc

irreversibly with the ion exchanger so it can be fouled. Organisms can grow in ion exchange beds necessitating the disinfection of these. However, when the turbidity is low ion exchange beds are used directly without a filter. At the end of the cycle the bed is backwashed and the fine turbidity passes with the water. If a bed becomes very fouled, resin cleaners are available. Condensates of high pressure boilers are purified with ion exchange beds, the main impurities removed are fine particulates of iron and copper. In some cases very finely ground ion exchangers are used as coatings on porous media for the removal radioactive species in particulate form usually derived from the materials of construction.

A study was made on the degree of particulate removal for given sizes of ion exchange particles. Fig. 1 indicates that the finer the particles, the greater the removal. But unfortunately, the finer the particles the greater the head losses (cf. Fig. 2). Another problem is that the very fine particles can not be backwashed or, if a mixed bed, it cannot be separated for regeneration resulting in increased costs due to the discarding of the resins.

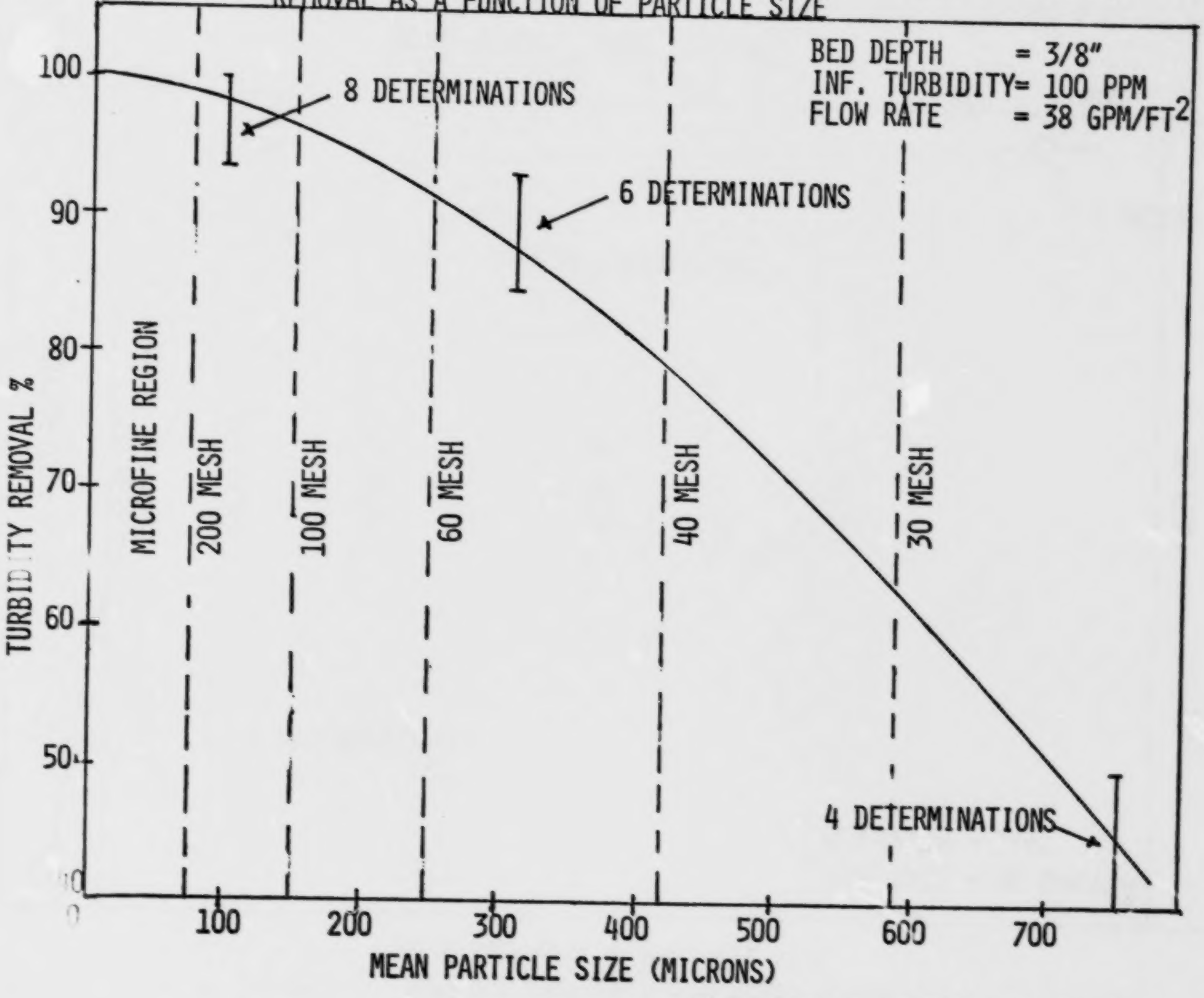
In several places the writer found the use of cation exchange beds as filters for particulates coming from poor piping or from local water supplies. The beds are only backwashed. The claim was made that they were superior to sand filters. There is a possibility of a charge formation on the resin component. If this be the case then active components could be built into the future filter media. A great deal of the effectiveness of sand filters is due to accumulated "debris" during the filtration probably due to polar groups present in the "slime".

Ion exchanger as carriers of reactants

Inorganic ion exchangers have been used now for sixty years as carriers of precipitated manganese dioxide for oxidizing Fe^{++} and Mn^{++} in low quantities in natural waters. The iron and manganese are precipitated and at the end of the cycle, they are backwashed. Regeneration is accomplished with a few ounces of $KMnO_4$ per cubic foot of bed.

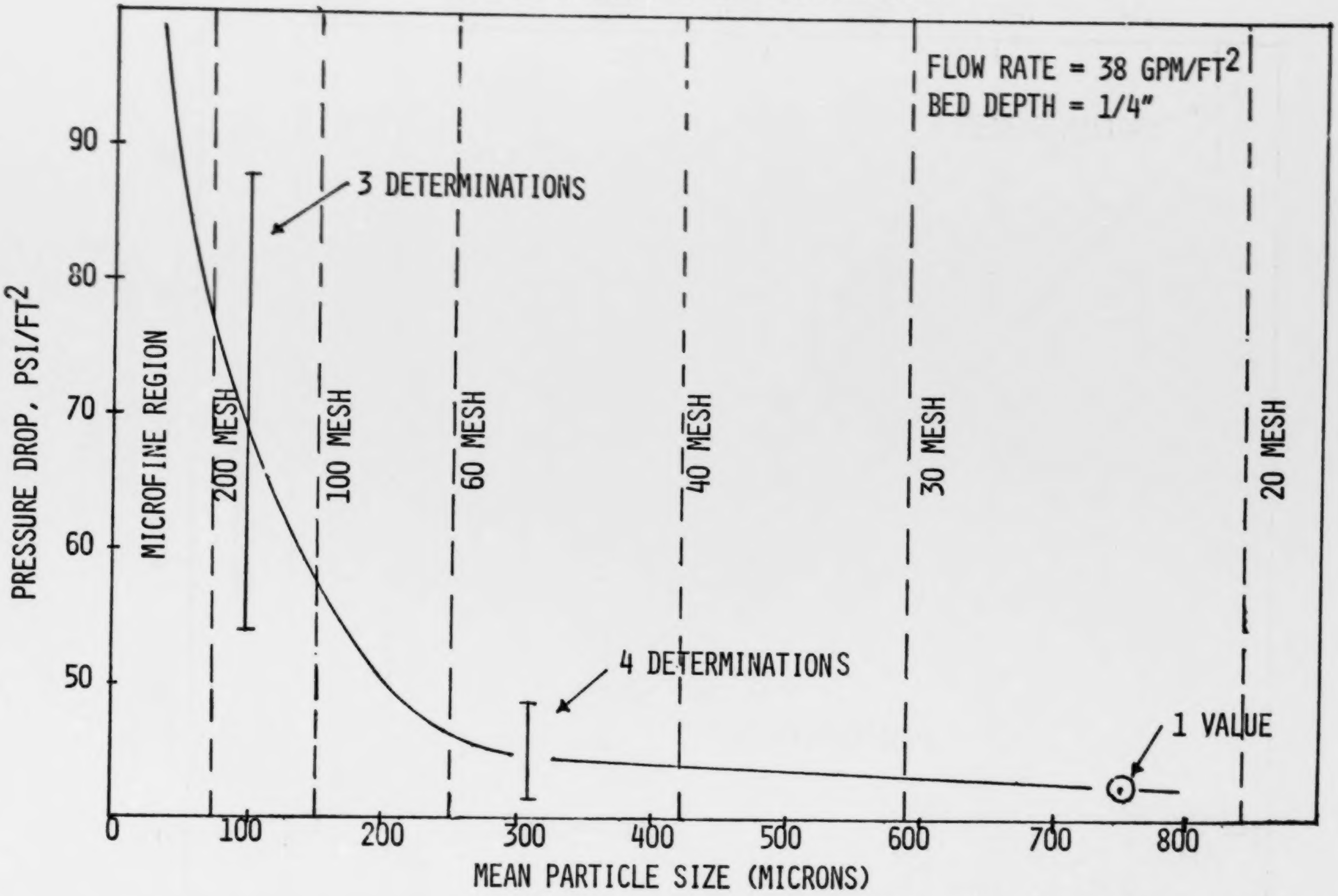
Another example of a reactant on an ion exchanger is the regenerated strong base anion exchanger with the sulfite ion for removal of oxygen from water. The sulfite is converted to the sulfate and when the bed is exhausted; it is regenerated with a sodium sulfite solution.

FIG. 1 SHALLOW BED PERFORMANCE OF H∽OH MIXED BED FOR PARTICULAR REMOVAL AS A FUNCTION OF PARTICLE SIZE



DATA BY G. P. SIMON & C. CALMON
IONAC CHEMICAL COMPANY

FIG. 2 PRESSURE DROP OF H∽OH MIXED RESINS
AS A FUNCTION OF PARTICLE SIZE



DATA BY G. P. SIMON & C. CALMON
IONAC CHEMICAL COMPANY

Thus, it is possible to utilize ion exchangers as carriers of reactants for specific applications.

Exchange to a more insoluble salt.

A very interesting patent for the removal of heavy metals, the sulfides of which are insoluble is that of Kraus and Phillips. (U.S. Patent 3,317,312, May 1967). It uses the sulfides as particles in a column through which the heavy metal ion is passed. If the metal ion in solution has a sulfide solubility less than the metal component of the sulfide in the column, it will exchange to form the more insoluble sulfide in the column. Thus, silver will be exchanged for iron when the iron is iron sulfide. Similarly, other metals such as cadmium, Bismuth, copper, mercury and gold can be removed in a similar manner. Table V gives the solubility of the more common heavy metal sulfides. The iron or manganese released can easily be removed with a manganese zeolite described above.

The particle sizes of the bed were in the range of 80-170 meah but small beds were found to be sufficient and the capacities were extremely high as the reaction appears to be with the bulk of the particles and is not limited to a reaction taking place on the surface of the particle.

This process is unique in that only the heavy metal ions are removed without the other ions being affected. Also, the iron or manganese released can be easily removed without producing much regenerant wastes. Also, the heavy metal is tied to a dry product which is insoluble. It can be discarded and if valuable can be readily recovered. This offers the possibility of valuable metal recovery from very dilute solutions. A cubic foot bed could treat 5 million gallons of water containing one ppm silver.

Ion Exchangers as Adsorbents.

While our past and present literature have many papers on activated carbon, activated alumina, silica and various gels as adsorbents, there is a limited literature on new organic adsorbents some containing anion exchange groups while others are polymers without polar groups. The former has extremely large pore radii ranging in size from 7,000 to 250,000 A° and a total ion exchange capacity of 4 meq/g. The resin is capable of being loaded with 2 to 3% of dry weight with colloids (R_2O_3, SiO_2 and organics). Recent work indicates that for humic acids, lignin sulfonates and anionic detergents, weak base macroreticular resins are applicable. For dye wastes strong base adsorbing resins appear to give best results. The latter is also good for humic acids when no detergents are present. For plating wastes containing non ionic detergents a macroporous adsorbing resin is recommended. Regeneration is accomplished with acid and caustic solutions.

TABLE V

Solubility of Sulfides

Metal Sulfide	Sulfide Concentration (Moles/1)
MnS	3.75×10^{-8}
FeS	6.1×10^{-10}
ZnS	3.46×10^{-12}
NiS	1.18×10^{-12}
SnS_2	3.1×10^{-13}
CoS	1.73×10^{-13}
PbS	1.84×10^{-14}
CdS	6.0×10^{-15}
Ag_2S	3.4×10^{-17}
Bi_2S_3	4.8×10^{-21}
CuS	9.2×10^{-23}
HgS	4.5×10^{-25}

The spent acid regenerant of such an adsorbent (Amberlite IRA-938) had in one case the following average analysis

Solids	9.1	grams/l.
SiO_2	0.3	" "
R_2O_3	1.9	" "
Organics	6.9	" "

Thus, the old view that ion exchangers will only react with ions in solution must be modified.

Resins with Chelate Groups

Several types of chelate resins exist on the market. The best known is Dowex A-1 which contains iminodiacetic acid groups ($R\text{-}CH_2\ N\ (CH_2\text{-}COOH)_2$) A recent announcement claims the preparation of a cross-linked aliphatic condensation resin with an amino and carboxyl groups (Seelex A-100) which is "specifically selective for cadmium".

Some claim that the chelation of these amphoteric resins is analogous in complexing tendency of ethylene diaminetetracetates but doubts exist that the mechanism is similar.

It appears some of the amphoteric resins have specificities for multivalent ions such as Cu, Ni, Co, etc.

The Dowex chelating Resin A-1 has the following selectivity sequence

$$Pd^{2+} > Cu^{2+} > Fe^{2+} > Ni^{2+} > Pb^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+} > Na^{+}$$

The chelate formation of the resin depends on the pH in the resin phase. Copper is picked up more at a lower pH. Complexing agents may be used as eluants.

Ion Exchange at elevated temperature and in presence of radiation

The initial ion exchangers were either synthetic sodium alumnio silicates or natural zeolites, glauconites or clays, such as the Bentonites. With the development of the synthetic polymeric ion exchangers the use of the former has become very limited to a few special uses. The first use of an exchanger for removing traces of a component in a mixture was by Folin at Harvard in 1917 for the removal of ammonia from urine with a synthetic sodium alumino silicate.

Most of the natural inorganic exchangers are cation exchangers. The only well known anion exchanger which is used for fluoride removal is apatite which comes from animal bone.

With the need for exchangers which will withstand radiation a whole series of amphoteric inorganics have been developed by combining group IV oxides with the more acidic oxides of V and VI. Thus, the oxides of Zr, Ti, Sn and Th can be combined with the acidic compounds of As, P, Mo and W. Unfortunately, the stability of these are limited to narrow ranges of pH. As they are resistant to radiation, they are utilized in some of the nuclear research centers where thermal and radiation stability is necessary.

Anion exchangers have been prepared from the oxide gels of Zr and Sn.

An alumino-silicate gel is used for removing Cs ions from waste and then carried as a solid to a point of use.

The molecular sieves which are crystalline sodium alumino silicates, with uniform pore diameters are used mostly as catalysts, adsorbents, and separation of organic molecules.

No doubt specificity exists in many inorganic exchangers which will be utilized. For instance, clinoptilolite is very specific for ammonia.

Ion Exchange Involving Selectivity.

The apparent selectivity coefficient is a good indicator of the affinity or preference of an ion exchange resin for a given ion over another. Thus, it becomes a good indicator in predicting which ion will be preferentially held by the exchanger. At this point, it must be pointed out that the greater the affinity of an ion, the more difficult it is to be removed through regeneration.

The selectivity of a resin depends on many parameters.

1. Solution concentration of the ion (e.g. HCO3 exchange for Cl in a anion exchange resin regenerated with NaCl).

Ratio of HCO_3 to total anions containing only HCO_3 and Cl	Ratio capacity of the exchanger for HCO_s^-
0.93	1.00
0.80	0.78
0.60	0.68
0.45	0.41
0.33	0.29

Softening is the removal of Ca and Mg at low concentration. A strong NaCl reverses the process, i.e., the Ca and Mg are released and the exchanger is converted in the Na form.

2. The valence of the ion--the higher the valence the greater the affinity (e.g. $N_a^+ < Ca^{2+} < Ce^{3+} < Th^{4+}$) For values see Table VI.

3. Solvation of the ion--the smaller the solvation equivalent volume the greater the affinity. (e.g. $Cs > Rb > K > Na > Li$). Variations have been found in some exchangers.

4. The cross linking of the ion exchange resin--the higher the cross the higher the affinity. (e.g., N. Copper and silver for a sulfonated copolymer of styrene and divinylbenzene with various cross linking).

Element/% DVB	4	8	12
Na	1.3	1.5	1.7
Cu	3.2	5.3	9.5
Ag	6.0	7.6	12.0

See Table VI for a selectivity coefficient of many heavy metal ions.

5. Polarizability of the ion--the higher polarizability the greater the affinity (compare Ag^+ against Na^+ although solvated volume and valence nearly the same).

6. Temperature--some resins reverse affinity with temperature (Sirotherm process based on it).

7. Pressure--Favors reaction which result in lower volume.

8. Interaction with fixed group or matrix: Ion pair formation --the stronger ion pair formation, the greater the selectivity.

9. Association of the ion with the same charge as the fixed ion with the opposite charged ion (e.g., in a mixture of $Na^+ + H^+ + CH_3COO^-$ the strong acid cation exchanger will prefer the Na^+, similarly Hg^{2+} is less preferred to other ions if Cl^- ions present in the solution).

10. Precipitate formation. If a precipitate forms then a less favored ion will be preferred (e.g., Ba^{++} in presence of SO_4 over Na^+, or Ag^+ in presence of Cl over Na^+).

11. Exclusion of very large ions in resins of limited pore sizes. This was already discussed previously.

Thus, for a large complexed metal cation a resin with a lower cross linking or high fixed porosity should be used.

12. Mole fraction composition--This varies also with the ions involved.

TABLE VI - Selectivity of Ion Exchange Resins*

Strong Acid Cation Exchanger (Styrene-DVB)

	Li^+ exch.				H^+ exch.		
Element	4	8	16	Element	4	8	12
Li	1.06	1.00	1.00	Li^+	0.9	0.85	0.81
H+	1.32	1.27	1.47	H^+	1.0	1.0	1.0
Na^+	1.58	1.98	2.37	Na	1.3	1.5	1.7
NH_4^+	1.90	2.55	3.34	NH_4^+	1.6	1.95	2.3
K^+	2.27	2.90	4.50	K^+	1.75	2.5	3.05
UO_2^{2+}	2.36	2.45	3.37	Rb^+	1.9	2.6	3.1
Rb^+	2.46	3.16	4.62	Cs^+	2.0	2.7	3.2
Cs^+	2.67	3.25	4.66	Mn^{2+}	2.2	2.35	2.5
Mg^{2+}	2.95	3.29	3.51	Mg^{2+}	2.4	2.5	2.6
Zn^{2+}	3.13	3.47	3.78	Fe^{2+}	2.4	2.55	2.7
Co^{2+}	3.23	3.74	3.81	Zn^{++}	2.6	2.7	2.8
Cu^{2+}	3.29	3.85	4.46	Co^{++}	2.65	2.8	2.9
Cd^{2+}	3.37	3.88	4.95	Cu^{++}	2.7	2.9	3.1
Ni^{2+}	3.45	3.93	4.06	Cd^{++}	2.8	2.95	3.3
Ca^{2+}	4.15	5.16	7.27	Ni^{++}	2.85	3.0	3.1

TABLE VI, Continued

Element				Element			
Sr^{2+}	4.70	6.51	10.1	Cu^{+}	3.2	5.3	9.5
Ag^{+}	4.73	8.51	22.9	Ca^{2+}	3.4	3.9	4.6
Pb^{2+}	6.56	9.91	18.0	Sr^{2+}	3.85	4.95	6.25
Tl^{+}	6.71	12.4	28.5	Hg^{2+}	5.1	7.2	9.7
Ba^{++}	7.47	11.5	20.8	Pb	5.4	7.5	10.1
				Ba	6.15	8.7	11.6

*Crosslinking 4, 8, 16% based on molar conc.

Beryllium is less than magnesium. Aluminum is less than ferric ion.

Weak acid cation exchanger (carboxylic)

$$H > Cu > Co > Ni > Ca > Mg > Na.$$

Weak Base anion exchanger (in Cl form).

$$OH^- > SO_4^= > CrO_4^= > AsO_4^= > PO_4^{\equiv} > MoO_4^= > Cl^-$$

Ion Exchange Through Specificity

This is one of the most interesting aspects in heavy metal ion removal as by means of specific resins it is possible to remove only the undesirable or recoverable ion and leave the innocuous ions in solution. This reduces the cost of regenerant, volume of waste, and can treat a large volume of water between regenerations. However, at present there are certain undesirable aspects.

1. Very few resins are specific to a single ion.
2. The rate of exchange is reduced.
3. The resin holding a highly preferred ion is difficult to regenerate.

In choosing a resin all the above parameters should be considered.

Table VII gives a list of known specific resins for various heavy metal ions.

It is this field which requires systematic studies for

1. Preparation of various resins with chemicals known to be specific for certain metal ions.

2. Evaluation of these for capacity, rate of reaction, and regenerant efficiency.

These resins could become important in recovering valuable metals even when in trace concentration. In fact, the Pyridinium resin is used to recover gold and then it is burned and the gold recovered. The users do not bother to regenerate off the gold with known solutions.

TABLE VII, Resin containing ion specificity

Element	Polar Group
Arsenic (3+)	Fluorone
Beryllium	Phosphonic Diallyl phosphate
Bismuth	Pyrogallol
Boron	N-methyl glucamine, tris hydroxymethyl amino methane
Cesium	Phenolic OH + Sulfonic groups
Cobalt	M-phenylene diamine, 8-hydroxyquinoline
Copper	Phenolic OH + phosphonic groups, 8-hydroxy quinoline m-phenylene diamine imino diacetic acid alginic acid
Germanium	Phorone
Gold	Pyridinium, thiourea
Iron	Alginic acid m-phenylene diamine hydroxamic acid phosphonous phorone chlorophyll haemin deriv.
Lead	Pyragallol, Phosphoric
Mercury	Thiourea, thiol, iminodiacetic acid, mercapto resins
Nickel	Alginic acid, Dimethylglyoxime
Potassium	Dipicrylamine

TABLE VII, Continued

Strontium	Phosphorous
Titanium	Chromotropic acid
Uranium	Pyridinium, phosphorous ester
Viruses	Metal cation proteins
Zinc	Anthranilic
Zirconium	Phosphate ester

Removal of Specific Heavy Metals from Water

Anodizing rinse waters, the aluminum is removed with a cation exchanger on the H cycle and the chromate in an anion exchanger.

Arsenic - has been removed as the arsenate with a weak base anion exchanger (Ionac A-260) in the Cl form.

Boron - removal from agricultural waters is possible at a cost of 12 to 30¢/1000 gallons (depending on size of plant) with N-methylglucamine resin, (amberlite XE-243) the regenerants are sulfuric acid and ammonia. In France, boron was removed by a long column of weakly basic resin.

Cadmium - Claim is made that a chelate Seelex A-100 containing an amine and carboxylic acid group is specific for cadmium. In plating rinse water standard cation exchange resins are used.

Cesium - Amorphous sodium, alumino silicate gel with a ratio of 1:1:6 is used for removal from some radioactive wastes and kept as such for long periods.

Chromium - As the chromate, it is removed with an anion exchanger. Trivalent chromium can be removed with a cation exchanger or it can be oxidized to the chromate and removed with an anion exchanger.

In cooling waters, if the reject contains 100 ppm of CrO_4, it is economic to use a highly basic anion exchanger which preferentially removes CrO_4 at a pH of 4.5 to 5.0 as at this pH the selectivity is $CrO_4 > PO_4 > SO_4 > Cl$.

Polychromates appear to form

$$R_2CrO_4 + H_2CrO_4 \rightarrow R_2Cr_2O_7 + H_2O$$
$$R_2Cr_2O_7 + H_2CrO_4 \rightarrow R_2Cr_3O_{10} + H_2O$$

To get a neutral chromate on regeneration

a) NaOH + NaCl are used as the regenerant.
b) It is followed by NaCl.

The dosages are

a) (2.5 lb. NaOH + 5 lb. NaCl) as a 10% solution
b) 5 lb. NaCl at 10% solution

Uptake of chromate is 7.7 lb./cu.ft. Recovered chromate on regeneraion 7.65 lb. or 99.7%. Effluent volume of Reg. is 6.5 gallons. Concentration of CrO_4 is 10% by int. The spent regenerant is reused in the cooling system.

Cost of regenerants are 5¢/lb. of CrO_4. Cost of Chromate per lb. 18¢, i.e. there is enough to pay for amortization and resin replacement.

The disadvantages are

1) Low flow rate. 2 gpm/cu. ft. of resin.
2) Resin can be fouled by organics & turbidity

Copper - See Plating Rinse Waters

Iron and Manganese - If in the divalent state, they are removed with standard cation exchangers in the sodium form.

If the two ions are in very low concentration (close to one ppm) they are removed with a MnO_2 carrier as explained before.

In condensate demineralizing the iron and copper which are either corrosion or erosion products are reduced to low values on passing the condensate through 3 ft. of mixed beds. Finely ground resins are used when the particulates are to be at extremely low value as in the case of radioactive components.

Gold - is removed today by anion exchangers, either a Pyridinium type or Type I basic resin. These resin are excellent when the gold is in alkaline or acid solutions. In highly acidic solutions the thiourea resin appears to be superior. But most gold wastes are alkaline solutions. The thiourea resin has a good capacity for platinum and iridium.

The capacity of the Pyridinium and Type I anion exchangers runs from 50 to 100 troy oz. per cubic foot of resin. Usually the resins are burned at 1000° C. and the gold recovered rather than regenerated.

The thicurea resin (SRAFION NMRR) appears the following capacities at the optimum pH of 0.5.

Gold	0.85	grams/gram dry resin
Platinum	0.50	" " " "
Palladium	0.30	" " " "
Iridium	0.30	" " " "
Rhodium	0.20	" " " "

There are 400 dry grams per liter of wet resin. The pH range of effectiveness is between 0.5 to 2.5.

If elution of the noble metals are desired a 5% aqueous solution of thiourea to which 5 ml. of HCl per liter of solution are added. The metal can be recovered from solution by reduction.

Mercury - Ionic mercury as well as Methyl mercury can be removed by a thiourea anion exchanger. The capacity was about 545 mg. Hg. per gram of dry resin. Regeneration can be accomplished with a 5% thiourea solution.

For mercury ion removal, wool may be used, the mercury probably complexes with the disulfite units of the wool. The capacity is approximately one mercury per disulfide linkage. Resins containing thiol (SH) groups have been prepared and applied to mercury ion removal. No doubt, the first reaction is ion exchange followed by complex formation.

A strong base anion exchange showed at a capacity of four pounds of mercury per cubic foot with a solution containing 15 ppm of ionic mercury. The effluent concentration was less than 0.01 ppm. The flow rate was kept at 2 ppm/cu. ft. Regeneration is with a strong acid and sodium chloride. About 25 lbs. of H_2SO_4 is used per cubic foot. The more dilute portion of the regenerant waste is recycled.

A Swedish ion exchanger (Q-13) appears to be highly selective for mercury. The chelate resin is made from a byproduct of sulfate pulp and has a capacity of one meq/g. If metallic mercury is present it is oxidized with chlorine to a pH of 6 to 7. The excess chlorine is removed with an activated carbon filter A bed with this resin has been in operation for nearly two years. With an extra unit as a polishing unit, the mercury is reduced to 0.1 - 0.2 ppm.

Nickel - See Plating Rinse Waters.

Plating Rinse Waters - The common ions in plating rinse waters may be Zn^{2+}, Cu^{2+}, Ni^{2+}, and Cr^{3+}. These are recovered with cation exchangers and the recovered metal ions on regeneration can be recycled or evaporated to the concentration needed. Hundreds of such plants are operating today very efficiently.

Platinum - See Gold

Radioactive Species - In particulate form these can be removed with ion exchange beds as described before. The ionic species are removed with mixed beds of ion exchangers.

The beds when exhausted are encased in cement and buried at specific storage areas. A patent is being issued on shrinking the volume of the ion exchangers by means of solvents so as to reduce the bulk storage volume.

By 1980 it is estimated there will be an annual consumption of 300,000 cu. ft. of ion exchange resin for removing radioactive ionic and particulate species from reactor cooling waters and pool storage waters.

Selenium - A combination of (a) sand filter (b) activated carbon (c) cation exchanger and (d) anion exchanger was used. The removal was (a) 9.5%, (b) 43%, (c) 44.7% and (d) 99.9% respectively. This indicates that some of the Se existed as a colloid and as an anion. The component removed by the activated carbon may be a complex.

Silver - Silver from plating rinse solutions can be recovered by passing the solution through a weakly acidic cation exchanger (H form) and then through a weakly basic anion exchanger (OH form), the silver cyanide complex is eluted with an alkaline solution of cyanide ions. If the silver is not complexed it can easily be removed with a cation exchanger.

Cost of Metal Ion Recovery

A theoretical calculation of the cost of metal ion recovery from solution by ion exchange has been made by R. Kunin in the Nov. 1967 issue of Amber-Hi-Lites. Although many assumptions were made as to the type and capacity of the exchanger, the type and quantity of regenerant and absence of interfering ions. But two columns in Table VIII give a key to costs which are worth reproducing:

1. Pounds of metal recovered per cu. ft. of resin, and
2. Cost of operation per pound of metal recovered.

Although the writer notes certain discrepancies in some cases involving actual plant operations, e.g.

1. In gold recovery the resin is burned so costs are slightly higher. The theoretical capacity is not far from the actual.

2. In Chromium recovery while cost is close to what is given in the table, the capacity is much higher in cooling water system due to complex formation on the resin.

However, it was indicated by Dr. Kunin that assumptions were made and also six years have added more data of operation.

Under the subject of Removal of Specific Metals from Water, four metal ions are worth discussing.

1. Boron removal at the cost indicated would be too costly for agricultural water, unless the product was costly. As boron is cheap and equivalent weight is low, the use of anion exchange process would have to involve an urgency of the production of a product.

2. Chromium removal in cooling water systems by ion exchange pays for itself when the concentration reaches 100 ppm CrO_4. In other words, it is a breakeven proposition so numerous plants have ion exchange recovery systems.

3. Cost data for mercury removal by the special resin (Q-13) are given by AKTIEBOLAGET-BILLINGSFORS for a 63,000 gallon per day plant with a water containing 10 ppm of Hg and 1% NaCl. The total cost is 53 cents per 1000 gallons; if credit is given for the reused acid and mercury, there is a net profit of 16¢/1000 gallons. However, no amortization cost for capital investments is given. It would appear that it is another breakeven system for a company which uses mercury in its processes.

4. Gold at the level today makes the burning of the resin worthwhile. If the capacity is 4 to 8 pounds per cu. ft. then the recovered gold is worth $4000 to $8000 while the resin is less than $100/cu. ft.

It would appear that all heavy metal ions should be checked on the degree of recovery and operation cost of the ion exchange systems available, especially for exchangers with the highest affinity, against the cost of the product on the market at a period with rising prices of many metals on the market.

Only strict laws or profits will drive industry to examine the available means of recovering wasted resources.

Comparison of Ion Exchange with Other Processes.

Ion Exchange is unique in that the lower the concentration of the metal ion the cheaper is the cost of treatment per unit volume of water treated.

In Electrodialysis, the lower the salt concentration the greater the resistance of the solution resulting in high power costs. In reverse osmosis as well as in evaporation and distillation, the cost of removing the water increases sharply with lower concentration of salts if viewed from the ions removed.

Secondly, frequently the metal ions recovered may be in a concentration which makes possible the reuse of the salt.

TABLE VII

Ion Exchange Capacity and Cost of Ion Exchange Operation For Metal Recovery

Cation Exchange

Metal Form	Capacity lb./cu.ft.	Cost cents/lb.
Al_2O_3	1.1	14
BeO	0.5	30
Cd	6.7	2.3
Ce_2O_3	5.6	2.7
CsCl	16.0	9.4
CoO	3.6	4.2
Cu	3.8	3.9
Pb	12.4	1.2
LiO	0.8	18
Mg	1.5	10
MgO	1.5	10
Mn	3.3	4.6
Hg	12	13
Ni	3.5	4.3
Ra	13.6	11
Rare Earths	6.3	2.4
Ag	13	1.2
Sn	7.1	2.1
Zn	3.9	38

Anion Exchange

Metal Form	Capacity lb./cu. ft.	Cost cents/lb.
Sb	4.5	6.7
Bi	3.1	9.7
Cr_2O_3	1.9	16
Ga	5.2	5.8
Ge	5.4	5.6
Au	7.3	4.1
Ha	6.6	4.9
Ir	7.1	4.2
Mo	3.6	8.4
Nb	3.4	8.8
Pd	3.9	7.8
Pt	7.2	4.2
Re	13.8	2.2
Rh	2.9	10
Ta	6.7	4.5
ThO_2	8.6	3.5
W_2O_3	6.8	4.4
V_2O_5	3.8	7.9
UO_2	8.8	3.4
Zr	3.4	8.8

Thirdly, the volume of regenerant is limited so that, if it is a waste, then the discarded volume is small.

Fourth, the particular metal ions may have a high selectivity coefficient or form a complex with the polar group of the resin sc that only the desirably metal ion is removed from solution while the innocuous ions pass untouched or are picked up to a limited extent. Thus, a greater purity of the metal ions may be obtained on regeneration.

The limitations of ion exchange are:

1) Fouling, especially of the anion exchanger in the presence of certain organic complexes. Pretreatments are available but it is an added cost.

2) Concentration of other ions may limit the capacity of the exchanger for the heavy metal ion if they have a selectivity close to the latter.

3) The volume of water treated is reduced as the concentration of the ion increases.

4) Regenerant wastes can be a problem.

However, the specific type of exchanger would overcome the above limitations and could be used for the removal of trace heavy metals from concentrated solutions.

This type of resin would offer a minimum volume of regenerant waste which today must be considered a liability.

For these reasons the writer believes that some systematic coordinated research work should be done in this field. This will yield the greatest economy in removal and may be a means of recovery of scarce valuable resources.

Mr. B. Fuller defines a pollutant as a wasted resource. With highly selective and well-defined specific ion exchangers the present heavy metal pollutants will be recovered or recycled resources.

ADDENDUM

Various aspects of ion exchange have not been mentioned. Therefore, these added notes are to make the subject more complete.

1. Ion Exchange membranes used in electrodialysis will be discussed in a later paper. E.D. units with ion exchangers in the compartment between the membranes are in use for the removal of trace radioactive nuclides from highly purified waters.

2. Data for the extraction of heavy metal ions with liquid ion exchangers are given in the analytical texts. The following heavy metal ions have been extracted with specific liquid ion exchangers (cf. Iczedy).

    1. Ac
    2. Al
    3. As
    4. Sb
    5. Ba
    6. Be
    7. Bi
    8. Cd
    9. CrO_4^{6+}
    10. Co
    11. Cu
    12. Ga
    13. Ge
    14. Au3+
    15. Hf
    16. Fe^{3+}
    17. In^{3+}
    18. Pb
    19. Mn^{2+}
    20. Hg^{2+}
    21. Mo^{6+}
    22. Ni
    23. Nb^{5+}
    24. Os
    25. Pd^{2+}
    26. Pt^{4+}
    27. Po
    28. Re^{7+}
    29. $Rn^{3,4}$
    30. Sc
    31. Se
    32. Sr
    33. Ta^{5+}
    34. Te^{4+}
    35. Th^{4+}
    36. Sn^{4+}
    37. Ti^{4+}
    38. Tc^{7+}
    39. W^{6+}
    40. $U^{4,6+}$
    41. $V^{3,4,5}$
    42. Zn
    43. Zr
    44. Y
    45. Lanthanides
    46. Transuranic elements

3. The redox resins may be used for oxidizing or reducing heavy metal ions in solution prior to analysis or ion exchange concentration.

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SOME EXAMPLES OF THE CONCENTRATION OF TRACE HEAVY METALS WITH ION EXCHANGE RESINS

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INTRODUCTION

Most heavy metals can be reduced to low levels in solution by the conventional techniques of precipitation and filtration. However, the concentrations remaining may still be above those that can be returned to the environment. These trace metals can be removed from solution by ion exchange. In some cases this will be technically or economically unattractive because of the other materials in the solution. However, it is often possible to transfer these metals selectively from a large volume of solution to a much smaller volume by the use of resins. The original stream, containing the bulk of the innocuous solids, then can be recycled or safely discarded. The heavy metals, having been concentrated into a small volume of solution, may be isolated by precipitation and filtration, or even distillation.

An ion-exchange column contains a set number of ionic or potentially ionic sites, each of which is capable of holding one ionic charge of the opposite sign under the proper conditions. The composition of the ions on the resin is controlled by mass action. That is, at equilibrium:

resin composition = f (solution composition)

All the ions of the same charge in the solution compete for the resin sites. If the solution contains a high ionic background, the selective removal under practical conditions of an ion present in very low concentration will require that the resin show a high selectivity for that ion. This selectivity may be optimized in some cases by altering the ionic background, or even just taking advantage f the ionic background present. The selectivity between monovalent and divalent ions is very dependent on total ionic concentration. With some heavy metals high concentrations of certain anions may actually drive the metal into the resin. A few examples will serve to show the diversity of approaches.

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ZINC IN COOLING TOWER BLOW DOWN

Two problems involving low levels of zinc have been studied in the laboratory. Different answers were obtained for the two cases.

A blowdown stream from a cooling tower contained approximately 6 ppm zinc which originated from the proprietary zinc-organic corrosion inhibitors used (1). The ionic background of the solution was:

	ppm as $CaCO_3$
Sodium	370
Total Hardness	84
Total Strong Acid Salts	385
Total Alkalinity	60
pH	7.5

The zinc level was to be removed from a 25 to 40 gpm stream to a level below 1 ppm and concentrated in a small volume for disposal.

The neutral pH and the presence of alkalinity in the stream suggested the use of weakly-functional cation exchangers. Such resins tend to show a higher selectivity for divalent ions over monovalent ions and more selectivity among the divalent ions than the strong-acid resins do.

Two resins were tried. A carboxylic resin, Duolite® CC-3, showed only a limited capacity for selective zinc removal. A phosphonic resin, Duolite® ES-63, proved to be very selective for zinc even over the other hardness ions present. The zinc in the column effluent was below the detection level (0.4 ppm) of the polarographic method of analysis used. Approximately 9,000 bed volumes of solution could be passed through the bed before zinc was detected in the effluent. The bed was regenerated with hydrochloric acid. The regenerant waste amounted to about six bed volumes. Thus the zinc was concentrated by a factor of about 1,500.

® Duolite is the registered trademark of Diamond Shamrock Chemical Company.

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ZINC IN KAOLIN WASH WATER

Another problem involving zinc ion occurs in the kaolin industry. Kaolin is treated with a solution of zinc hydrosulfite to reduce and solubilize the iron present for color improvement. About one pound of zinc is used per ton of kaolin processed. The annual rate of kaolin production was roughly 4 x 10^6 tons in 1972. Most of the zinc is washed out of the kaolin. The raw water has a low solids content and is relatively soft. The used wash water has a pH of 3.0 to 3.5, contains variable amounts of zinc, and has a low ionic background. This waste currently is blended with other plant wastes, neutralized with lime to a pH of 5 to 6, and ponded before discharge. Even so, plant effluents may contain from 10 to 60 ppm of zinc. The kaolin producers have been told to find means of reducing the effluent zinc to well below 1 ppm.

A weak-acid exchange resin is the first choice for the concentration of a heavy metal from dilute solution because of the high efficiency with which it can be regenerated. However, such a resin does not seem to be applicable to this zinc problem. The weak-acid exchange resins do not show a useful operating capacity until the pH of the solution is at least 5 to 6 pH. At this pH a portion of the zinc exists as insoluble zinc hydroxide. This would require prefiltration of the total volume of waste. The flow rate through the resin would have to be relatively slow, so a large inventory of resin would be required. There would be a double neutralization expense in that the acidic waste would have to be adjusted from 3.5 to 6pH before ion exchange, but would come out of the ion exchange at 2 to 4 pH and would have to be neutralized again before it could be sewered.

The low solids content of the wash stream makes a conventional sodium-softening cycle using a strong-acid resin attractive for the removal of zinc in this case. A synthetic waste water was made up in the laboratory to simulate the kaolin wash water prior to liming. The analysis was:

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Zinc	42 ppm (as zinc)
Sulphate	90 ppm (as $CaCO_3$)
Chloride	12 ppm (as $CaCO_3$)
Calcium	20 ppm (as $CaCO_3$)
Magnesium	24 ppm (as $CaCO_3$)
pH	3.7

This water was passed through a 2.5 cm I.D. column filled to a depth of 92 cm with Duolite® C-20, sodium form. The flow rate was 25 bed volumes per hour. No zinc was detected in the effluent (detection limit 0.4 ppm) until after 1000 bed volumes had passed through. There was a minor leakage of hardness before this point, but the zinc and hardness both broke through at essentially the same time. The capacity of the column for zinc under these conditions was 1.3 equivalents per liter.

This cycle has several attractive features. A high flow rate can be used, so the resin inventory is reasonable. No pH adjustment of the solution is required prior to ion exchange, as the softening cycle will work as well at 3 pH as at 7. In fact, the sodium cycle exchange will give some acid neutralization for at least part of the cycle.

Regeneration with a high level of concentrated sodium chloride (300 g/liter as 20% solution) elutes the zinc well enough even with conventional downflow operation that zinc leakage in the following run is below detection by the analytical method used. Even at this high regeneration level the volume of regenerant effluent is 3 volumes per volume of resin or less. If the bed treated 1000 volumes, this would represent a concentration factor of 300 to 400 fold. The heavy metals could be precipitated from this small volume of solution by adjusting the pH to 8.5. The residual brine could be metered back into the untreated waste stream so that any zinc left unprecipitated is again picked up by the ion-exchange unit.

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LEAD IN PLANT WASTE STREAMS

Kozak, Baczuk and Landram have reported on an investigation of the removal of lead from waste streams from an ammunition plant. (2). The plant effluents were found to average 6.5 ppm of lead while the proposed tentative standard was a maximum of 0.05 ppm. The lead could be reduced to 0.1 ppm or slightly less by careful precipitation. A number of different types of ion-exchange resins were investigated. The only one which gave a satisfactory performance was the phosphonic acid resin, Duolite® ES-63. This resin routinely gave effluent levels of 0.01 ppm of lead or less. The resin was regenerated with nitric acid to give a solution containing about five percent lead, a concentration factor of over $5x10^4$ based on the concentration entering the ion-exchange step.

The pH of the influent stream was shown to be critical. If the pH of the influent was above 5.2, a portion of the lead was present as a colloid and slipped through the bed without being exchanged. If the pH is much below 5, the available exchange capacity of the resin will be reduced. The final recommendation of the study was a precipitation step with lime and ferric salt to remove 80% of the lead, and Duolite® ES-63 to bring the final discharge to below 0.05 ppm.

CHROMIUM IN COOLING TOWER BLOWDOWN

Many heavy metals form stable complex anions in solution. Chromium is routinely concentrated by anion exchange when present as the chromate or dichromate. Chromates are commonly used inhibitors in cooling towers. The blowdown streams from these towers may contain from several hundred to a couple of thousand ppm of dissolved chlorides and sulfates. These streams are essentially innocuous except for a low level of chromate ion, usually less than a hundred ppm. If the blowdown stream is adjusted to a pH of approximately 5 and passed through a strong-base anion-exchange resin, the chromium is retained and the bulk of the other ions pass through (3). The resin is regenerated with an alkaline

.../...

salt solution. The resulting solution of chromate and salt is concentrated enough that it can be returned to the cooling tower.

Again in this system pH is a critical factor. If the pH is below 4 the oxidizing power of the chromic acid starts to attack the resin. If the pH of the stream is above 6 the ratio of chromate to dichromate in solution increases. The resin is apparently less selective for the chromate ion than for the dichromate ion and early leakage of chromium occurs.

MERCURY FROM BRINE

Many of the heavy metals form anionic complexes that, although transitory in solution, are tightly held by strong-base anion exchangers. This phenomenon has been investigated for most of the elements in chloride and several other types of backgrounds, initially by Kraus and co-workers (4). The extent of pickup is a function of the particular cation, the nature of the complexing anicn, and the concentration of the anion. Two commercial applications of this type of ion-exchange are the removal of trace amounts of iron from concentrated hydrochloric acid and the recovery of low levels of uranium from sulfuric acid leach solutions.

A strong-base anion-exchange resin shows a high affinity for mercuric ion over a broad range of chloride ion concentrations. A process for the removal of mercury frcm the spent brine from a chlorine-caustic electrolysis cell with a mercury cathode was developed in the early 1960's (5). Passage of the spent brine through the resin reduced the mercury level to below the detection limits then in use. Since the affinity of the resin for mercury actually increases as the chloride concentration decreases, it was desirable to reduce the mercuric ion to mercurous ion on the resin with thiosulfate in order to recover it (6). The recovered mercury could be returned directly to the

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electrolysis cell. This process was evaluated at pilot-plant scale and found to be technically feasible. Since the only motivation for its implementation at that time was a possible savings in mercury costs, it was not financially attractive enough to be installed.

Understandably, there has been a renewed interest in the use of ion-exchange resins to remove mercury from chlorine-caustic cell wastes in the last five years. It is unlikely that the above process would be a completely satisfactory solution to mercury cell problems under the present standards of discharge as monitored by newly developed analytical methods. The pick-up of mercuric-chloride complex on a strong-base resin is more in the nature of an adsorption process than a true ion-exchange. An adsorption curve can be determined showing that the amount of mercury that can be loaded on the resin is a function of the equilibrium concentration of mercury in solution, much as in the adsorption of a solution on carbon (Fig. 1). If only trace amounts of mercury are present in the solutions to be treated, the resin will show a low effective capacity and leakage is probable. The strong-base resins would thus be excellent for removing 99% or so of the mercury, but they alone would not give a satisfactory answer.

A number of ion-exchange resins were recently screened for their ability to adsorb mercury. Resins based on a phenol-formaldehyde polymer were found to have activity (Fig. 2). Those resins with phenolic, carboxylic or sulfonic functionality had a rather low adsorptive capacity. However, when some weakly-basic groups were present, a very worthwhile capacity was obtained. The capacity is of an adsorptive nature, and, unlike with the strong-base resins, a chloride background is not necessary. The mercury can be regenerated from the resin with hydrochloric acid. These resins offer another method of removing the major part of the soluble mercury from an aqueous stream.

Mercury adsorption resins have been offered recently that retain a high capacity even at very low mercury concentrations in the contacting solution. These resins are phenol-formaldehyde or styrene-divinylbenzene structures containing sulfur, probably as sulfhydro groups. These resins show flat adsorption isotherms and should be quite effective in

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removing mercury to extremely low levels. They are stated to be unstable to oxidative conditions. Chemical regeneration is difficult. This type of resin will be most useful as an expendable adsorbent to remove the last traces of mercury after the majority of the mercury has been removed on a regenerateable resin bed.

SUMMARY

When considering the problem of concentrating a heavy metal from solution, a large number of interrelated factors must be considered. A partial list will include:

- the metal
  - initial concentration
  - final concentration required
  - oxidation state
  - solubility versus pH
  - tendency to form complex ions
- the solution
  - volume per unit time
  - disposal or recycling requirements
  - pH
  - extraneous salts
    - concentration
    - nature
  - temperature
  - oxidative or reductive potential
- allowable costs
  - capital
  - operating
  - alternatives

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Usually the most difficult step is getting the man who understands the problem and has most of the above information, together with a man who has the necessary specialized background and experience so that between them they may come up with a workable answer.

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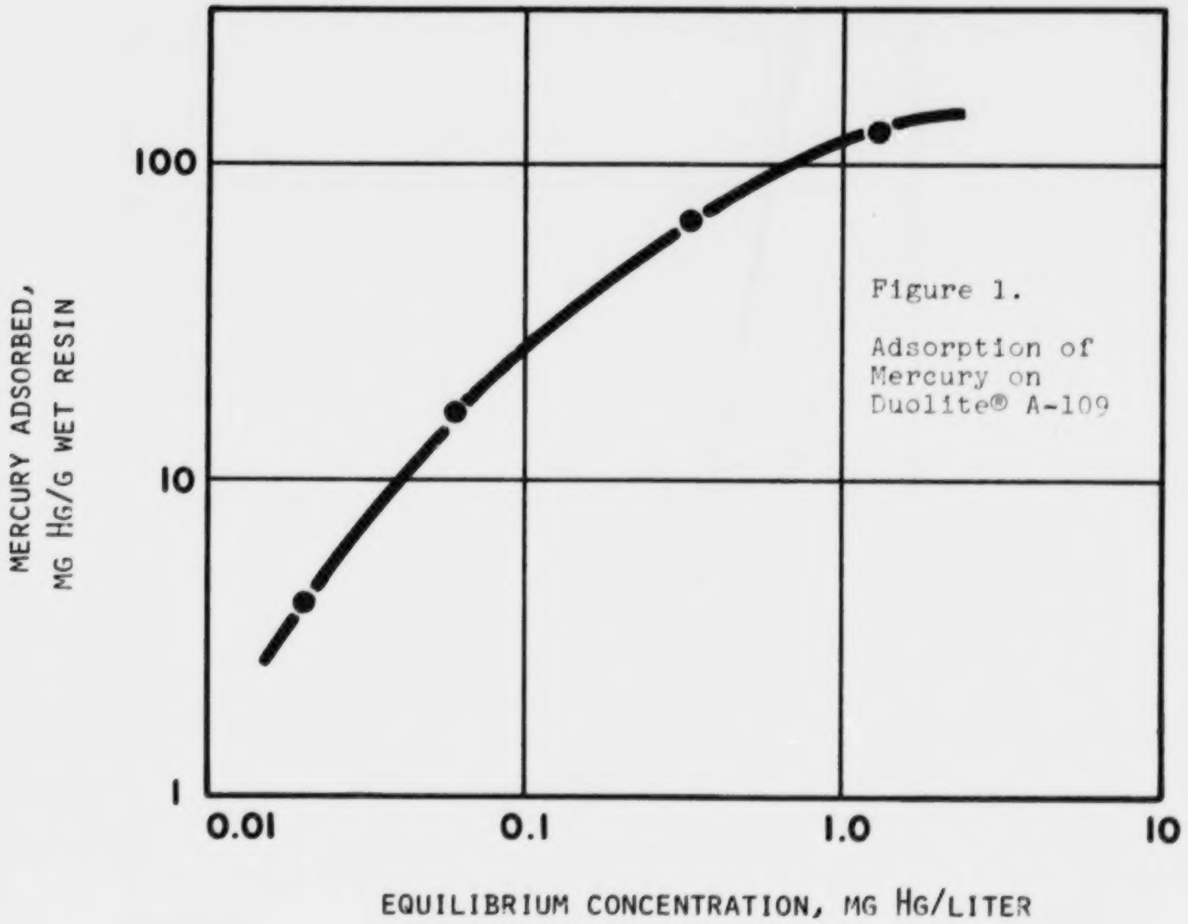

Figure 1.

Adsorption of Mercury on Duolite® A-109

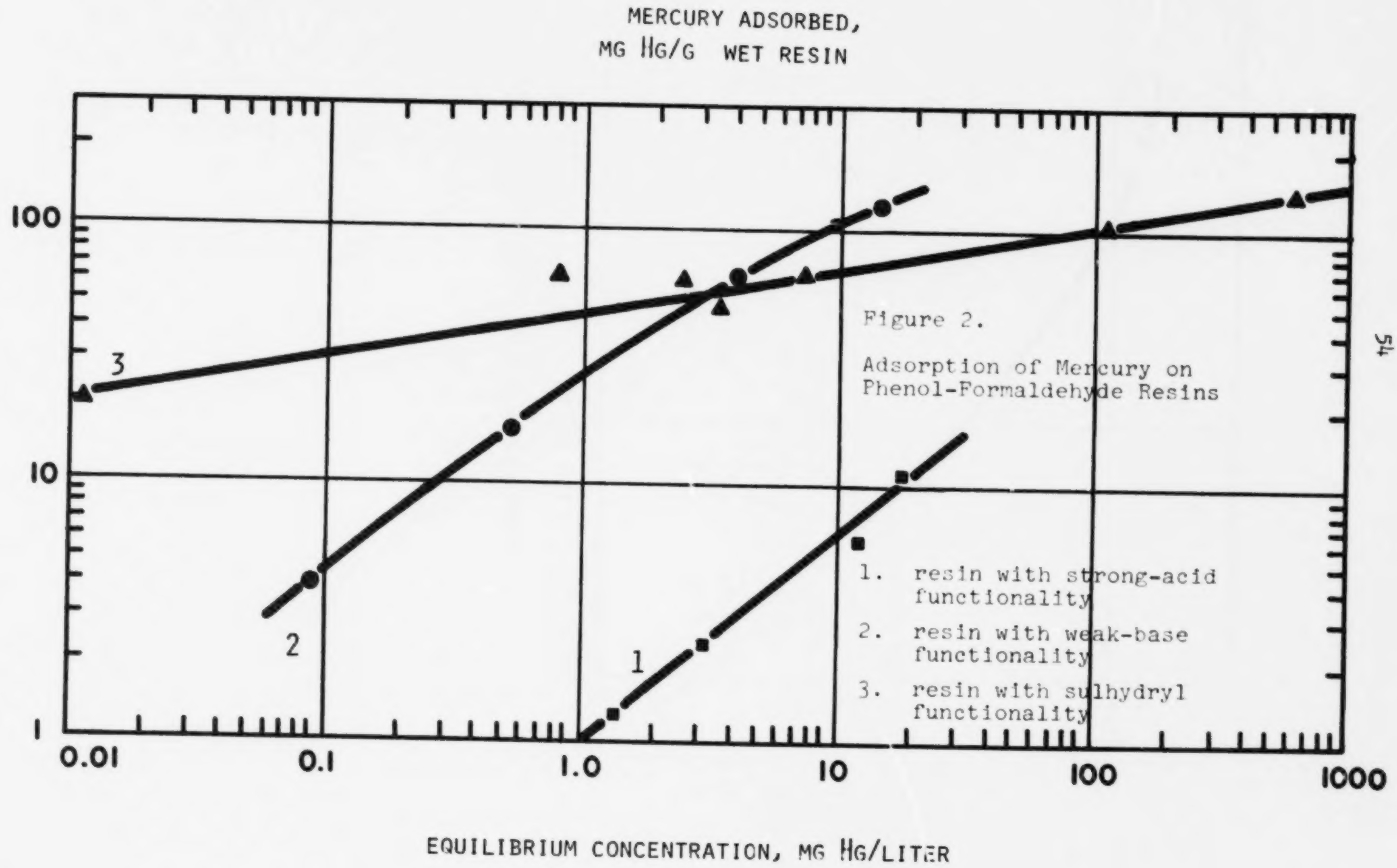

Figure 2.

Adsorption of Mercury on Phenol-Formaldehyde Resins

TRACE METALS REMOVAL BY ACTIVATED CARBON*

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BACKGROUND

Adsorption is a phenomenon long recognized for its value in scavenging and retaining soluble materials even at extremely low concentrations. Adsorption will usually take place in very low concentration ranges where other processes such as precipitation or ion exchange become ineffective. It is only natural then that adsorption should be given a chance to demonstrate its usefulness in the removal of trace heavy metals in solution and that activated carbon, the most effective adsorbent in aqueous media, should be given a thorough evaluation.

Activated carbon, though well known for its ability to adsorb organic vapors and organic impurities, such as color, aromatic compounds, and the like from aqueous solution, is not generally recognized as an effective adsorbent for ionic species. Nevertheless, the ion exchange properties of activated carbon were recognized many years ago and studied in some detail by Steenberg(1). Oxygenated surface groupings of various types were found to be present and would react with cations to form salts and a definite displacement series could be worked out for various ions on carbon, quite analogous to the case of resins. These surface groups may be either maximized or eliminated by thermal treatment of the carbon in controlled atmospheres. However, these surface complexes have been, until recently, regarded as of secondary importance to the surface area and pore structure of the carbons which govern the adsorption of non-polar substances.

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*Presented at the Conference on Traces of Heavy Metals in Water: Removal Processes and Monitoring, at the Center for Environmental Studies, Princeton Univ. Nov. 15-16, 1973.

EARLY METALLURGICAL APPLICATIONS

One of the earliest practical applications of adsorption of metals was in the recovery of gold and silver from ore pulps in the presence of cyanide. The cyanide dissolved the metal from the ore and the activated carbon adsorbed and concentrated the metal as a cyanide complex. Other metallurgical uses have been developed in the adsorption of molybdenum blue, vanadium and uranium.

Aside from metallurgical uses there was little interest in the adsorption of metals at trace concentrations. Over the years, Hassler(2) and his associates at Westvaco (then West Virginia Pulp & Paper Co.) conducted a number of laboratory studies on the adsorption of various metals and inorganic ions. Under the right conditions of pH and oxidation potential, certain metals were found to be adsorbed very strongly and in large amounts. Other ions might be adsorbed either very slightly or not at all. The entire range of the periodic table and infinite combinations of pH, oxidation states and dissolved salts in the medium presented a formidable task for any thorough investigation. Nevertheless, a number of systems were studied and a general article on the possibilities of the adsorption of inorganic compounds was recently published(3). Also to promote the use of activated carbon in metallurgy a special study was sponsored by Westvaco at Colorado School of Mines Research Foundation. Though this work was not aimed toward trace metal removal, it was found that good adsorption of metals could be obtained if these were in the form of ionic complexes of high molecular weight or in non-polar forms of limited solubility. The adsorption of the vanadium(4) was studied in some detail and a recovery scheme developed employing activated carbon. At about this same time a process for concentrating and purifying Mo was being developed by a mining company involving the adsorption of molybdenum blue; an inorganic polymeric complex of Mo oxides. At this point there was little interest in adsorptive removal of traces of heavy metals except as it contributed to the efficiency of metallurgical recovery.

MERCURY REMOVAL BY ACTIVATED CARBON

In 1970, the nation became alarmed about the widespread contamination of surface waters by mercury when mercury cell chlorine/caustic plants were found to be losing large quantities of mercury in various forms into streams used for potable water sources. One caustic manufacturer, Canadian Industries, Ltd., was already studying this problem and had obtained a patent(5) on carbon columns to remove mercury from caustic. The adsorbing and filtering action of the carbon was supplemented in their filter design by layers of metal turnings or gauze to retain free metallic mercury by amalgamation. Westvaco and others set up column and batch contacting studies to determine the most effective way to remove mercury in its various forms with activated carbon. From this and other work it was learned that filtration through combinations of coarse powdered activated carbons and cellulosic filter aids was very effective in removing mercury from caustic down to very low levels, e.g.,< 50 ppb. A number of carbon filters of various types were set up in this country and Canada for treating caustic solutions and mercury bearing waste effluents. A paper(6) covering field applications of this type was given by the writer at the WPCF meeting in 1971. These filters, to our knowledge, were the first carbon installations for the sole purpose of trace metal removal. The mercury was initially present in such forms as metallic droplets, possibly emulsified, mercuric and/or mercurous salts and as organic compounds such as methyl mercuric chloride or dimethyl mercury and yet all were removed to a high degree. Thus, it was obvious that several removal mechanisms must therefore be involved.

It may be well to emphasize at this point that the very reasons why carbon is appealing for mercury removal also make it attractive for the removal of other trace metals. These reasons are:

1) Carbon is an effective removal agent even at very low solution concentrations
2) The removal action is relatively non-specific, that is, the carbon has a capacity for the metal in several different forms
3) Carbon may be regenerated for reuse by acid washing and/or thermal treatments and the metals recovered, if of value.

MECHANISMS OF REMOVAL

In order to put the phenomenon of physical adsorption into proper perspective and to differentiate between this and "real" removal processes on activated carbon it may be helpful to discuss some of the possible mechanisms for heavy metal removal.

1. True Adsorption - In theory only true solutions are acted upon by classical adsorption. The dissolved adsorbate is attracted to the gross interior surface of the carbon and establishes a dynamic equilibrium between a concentrated surface layer and a dilute solution in the pore space. All portions of the surface, amounting to as much as 1200 m^2/g are involved provided the pores within which some of the surface lies are not inaccessible to the adsorbate due to size consideration. The surface will be very non-uniform and the more tenacious adsorption will take place in the finest pores and most active parts of the surface resulting from unsatisfied valence bonds, surface charges, etc. In an aqueous media the entire surface will be saturated with water but this is easily displaced from the hydrophobic carbon surface except where hydrated surface groupings are attached.

True adsorption will occur most efficiently for large molecules with a minimum of surface charges and low solubility.

2. Precipitation - There is a thin line of distinction between true adsorption and precipitation on the surface. However, if a material of very low solubility is present, a drop in temperature, the addition of other substances, etc. may cause the solution to become supersaturated. Activated carbon can provide a potent nucleating force causing a precipitate to form on the surface until the supersaturation is removed. Then additional material may be removed by adsorption to reach still lower concentrations in the surrounding solution.
3. Ion Exchange - All commercial activated carbons contain some functional groups containing oxygen on the carbon surface. Since the basic carbon skeleton is graphitic in nature, phenolic, carboxylic, ether, peroxide, lactone and hydroxyl groups may exist. The total number and type will depend on the thermal history of the adsorbent and on the oxidants to which it has been exposed. Other groups containing sulfur and nitrogen may also be present. Some of these groups will form salts as in the case of ion exchange on resins. The exchangable sites act in analogous fashion to those in ion exchange resins and various metal cations will displace each other in a predictable fashion. Most such groups are cation acceptors though some anion acceptors may also be present. In general, the number of such groups is uncontrolled in commercial activated carbon but products from certain processes will tend to have a more or less typical surface group distribution. Such groups are fast acting and are responsible for removal of the simple metal ions in the 1, 2 or 3+ valence states. Purposely oxidized carbon will have a maximum of such activity.

4. Reduction to Metal or Oxidation to Insoluble Forms - The carbon surface is an active catalyst for both reduction or oxidation depending upon the surrounding medium. In the presence of dissolved oxygen, ferrous ion is quickly oxidized to ferric ion and this is readily precipitated as $Fe(OH)_3$ if the pH is 4 or over. Likewise, reduction can take place if reducing agents are present. Various impurities such as elemental iron, ferrous salts and sulfides may be present in trace amounts which can reduce metal ions such as silver, gold or mercury to elemental form.
5. Filtration or Entrapment - A granular bed or a cake of fine carbon can act as a very effective filter. Suspended particles will cling to the rough carbon surfaces and coagulation of suspended or colloidal matter can be induced by the strong surface forces surrounding particles which can remove surface charge layers and break up emulsifier layers.

With the existence of these many surface phenomena it is very difficult to predict what will take place in a real trace metal problem situation. With this as background, current developments in the application of activated carbons may be more meaningfully discussed.

REVIEW OF RECENT DEVELOPMENTS

Direct Adsorption - This classification is meant to consider simple treatment of a stream containing metals by applying commercial activated carbons in either granular or powdered form without prior addition of reagents to either the solution or the carbon. A review of abstracts over the past five years reveals the removal of the following metals in varying degrees.

Chromium as chromate at 100 ppm was 80-85% removed from electroplating waste by coal base activated carbon according to a Japanese investigation(7).

Lead, Ni and Cd were adsorbed on both regular and oxidized carbons from solutions of alkali metal chlorides to reduce impurities to the $2\times10^{-6}\%$ level as determined by a Russian group(8). Other metals were also removed including Zn, Fe, Mn, Ca and Al.

Another Russian group(9) reported strong adsorption of Bi, Mn, Cu, Zn, Cd and Pb from hydrochloric acid solution and a method of quantitative separation of binary ion mixtures was proposed.

Germanium(10) has been quantitatively adsorbed in an expanded bed of granular wood base carbon. The adsorbed metal was quickly removed by washing with 1% NaOH. In addition to the articles already mentioned there are a number of references to mercury removal.

A Russian article(11) reports adsorption of mercury from waste waters on activated charcoal followed by regeneration by heat treatment in a vacuum yielding condensed Hg in a cooled zone. Carbons with hydrophobic surfaces were found by a Polish researcher(12) to be superior adsorbents for mercuric chloride. Mercuric chloride(13) was found to be well adsorbed by a number of Russian commercial carbons and kinetics were studied by a Russian group.

The most directly applicable data for potable water treatment for Hg removal consists of two articles by Gary Logsdon and James M. Symons at the Water Supply Research Lab. in Cincinnati. In this work(14) which covered the comparative effectiveness of conventional water treatment methods in removing mercury, granular activated carbon was found to be most effective in removing organic mercury and powdered carbon was found almost equally effective in removing both organic and inorganic mercury. Though a variety of mechanisms of removal appear possible, such as ion exchange or sulfide precipitation, true adsorption appeared to be the most likely mechanism in that reasonably well-defined Freundlich isotherms with slopes less than one were obtained. Also, the column tests showed evidence of greater loadings due to the countercurrent contacting, i.e., saturation at the high influent concentration level.

In a more recent paper(15) Logsdon and Symons described similar work with As^{+5} Ba^{+2} and $Se^{+4,+6}$. In this case activated carbon in powdered form was poorer at removing these elements than were coagulation or softening. Further work is planned on cadmium, chromium and lead.

There is also work underway on the effect of powdered activated carbon in combination with conventional secondary sewage treatment practices for the purification of industrial waste. Data are being collected on the following metals, Ni, Fe, Cr, Hg, Pb, Cu, Zn, Mn. Though high degrees of removal have been observed on certain metals it is not clear at this time whether the carbon is mainly responsible. At present these data are regarded as confidential, but hopefully they will be correlated and released within a reasonable time.

Adsorption of Complexes - The adsorption of metal complexes has been known for a number of years and the adsorption of silver and gold as cyanide complexes has already been mentioned. Soon after EDTA came into use as a chelate for calcium and other metals it was found that the metal chelates were easily adsorbed. It was also found, however, that if the EDTA were preadsorbed on the carbon it unfortunately lost most of its chelating efficiency. According to a recent reference, J. Leontiades(16) has used the adsorption of the chromium EDTA complex to increase the sensitivity of a radiochemical detection device. Further work on gold and silver has been reported by Taskin(17)(18) and Nizamutdinova(19). High capacities for gold are also reported by Lodeishchikov(20) in strong thiourea solution obtained from stripping ion exchange resins used to pick up a variety of metals.

A highly efficient adsorption of the nitratonitrosyl and nitronitrosyl ruthenium complexes are reported by Matsumura(21) and adsorption of yttrium in the presence of humic acid has been reported by Shchebetkovskii(22) Some work has been done by Westvaco on the adsorption on metallic salts of modified soluble lignins as a means of stripping out traces of heavy metals. This technique holds promise and will be investigated further.

In summary, the surface has only been scratched on the possibilities of adsorption of metal complexes. The technique should certainly be tried on specific problem metals if direct adsorption or other methods fail.

Metal Removal by Modified Carbons -

Oxidized activated carbons - In the last five years considerable work has been done with carbons with specially prepared oxygenated surfaces. Such carbons have been prepared by heat treating them in oxygen-containing atmospheres or by exposing them in slurry form to oxidants such as nitric acid. Apparently the ion exchange activity of the carbon can be greatly enhanced by this means. Tarkovskaya(23) reported in detail on a carbon oxidized in air at 400-450°C. Dynamic sorption capacities ranging from 0.16 to 0.86 meq/g at a pH of about 4 were observed for Na^+ and Fe^{3+}, respectively. A displacement series was worked out for 13 cations at pH 1-6. Selectivity factors were also determined for various pairs of cations. Purification processes were suggested for metal salts and hydroxides of the alkalis, with removal of Mg, Al, Zn and Ni requiring treatment by 0.5 to 5% of the oxidized carbon in a single operation.

Kononchuk(24) used a nitric acid oxidized carbon in the sodium form to purify the mother liquor from chlorine production and reports the capacity to be higher than commercial carboxyl and sulfonic acid cation exchanges. Metals removed were Mg, Ca, Cu, Pb and Fe. Another Russian investigator, Taushkanov(9) cited earlier, also reported the purification of alkali metal chlorides by oxidized carbon and found that oxidation greatly enhanced the activity of the carbon. Impurities in NaCl solution consisting of Al, Ni, Zn, Fe, Pb, Mn, Cu, Ca, Mg and Ba were reduced to 2-3 x 10^{-6}% (20-30 ppb) for each element.

To my knowledge, no purposely oxidized carbons are produced commercially in this country, nor is there commercial process employing such carbons. If purification processes involving heavy metals are going to be required in the future perhaps oxidized carbon should be developed commercially to compete with ion exchange resins. These are currently acid washed granular carbons on the market but these are not in great demand. Their principal use is in acid systems where the leaching of inorganic impurities from the carbon would be detrimental.

Metal removal by impregnated or "loaded" carbons - Since it was learned that metal complexes could be strongly adsorbed on activated carbon a number of investigators have been intrigued with the possibility of adsorbing specific chelating or complexing agents onto carbon and thereby obtaining a specific adsorbent for a particular metal ion.

In 1967, Egorov(25) reported on the addition of pyrocatechol and similar compounds to increase the adsorption of germanium.

Plyushcheva(26) in 1969 reported on the use of carbon loaded with dimethylglyoxime to remove Ni, La, Co and Fe ions. Also studied were carbons loaded with Trilon B and citric acid. The response of the adsorption to pH changes indicated that the sorption capacity corresponds to the stability of complexes formed by the ions. In 1970, Evdokimov(27) published data on the separation of Ge^{4+} and As^{3+} on carbon treated with tartaric acid and ferric hydroxide. Tartaric acid pushes the selectivity toward Ge whereas the $Fe(OH)_3$ favors As^{3+} sorption. Later the same author showed that Ge adsorption is also increased by loading citric acid(28) onto the carbon and Ge removal is in stoichiometric proportion to the citric acid added. With o-hydroxyquinoline it was learned(29) that As would only be adsorbed when Ge was present suggesting Ge-As compound formation when the two are adsorbed together.

In 1971, Plyushcheva(30) reported further work with dimethylglyoxime and also hydroxyquinoline, diethyldithiocarbamate and citric acid in the adsorption and purification of La, Ni, Co and Fe.

In this country the most significant work appears to be that of R. H. Moore(31) of Batelle Memorial Institute under the sponsorship of Office of Saline Water of U. S. Dept. of the Interior. This work had as its objective the removal of Cu from sea water desalination plant effluent. Eight chelating agents and six activated carbons were evaluated. The most useful chelating agents were: salicylaldoxime, 8-hydroxyquinoline, benzoylacetone, dibenzoylmethane, anthranilic acid and mercaptobenzothiazole.

This presentation is a most significant one in that it establishes the practicability of loading carbons with a reagent of reasonable cost and applying it in a cyclical fashion to a real problem. Both hydroxyquinoline and salicylaldoxime may be used on standard granular carbons of several types and used to remove copper from dilute or more concentrated solutions to levels of 10 ppb or less until an abrupt breakthrough is reached. Though only between 46 and 80% of the theoretical chelating capacity was realized it was found that substantial amounts of "direct adsorption" on the base carbon were obtained as well which were not affected by the reagent adsorbed on the carbon surface. This "direct" adsorptive or ion exchange capacity led to combined Cu removals as high as 187% of theory. The sorbent could be easily regenerated by acid wash. However, the direct adsorption by carbon itself was unable to remove low concentrations of copper which were easily, though more slowly, taken up by the chelating reagent.

The regeneration of the saturated sorbent was found very practical though the "working" capacity of the second and higher cycles were not as high as the initial adsorption. Both the chelating capacity and the carbon activity could be regained with a reasonable quantity of regenerant. A slight leakage of reagent in either the unreacted or metal loaded form could be contained in a small guard bed of pure carbon downstream.

SUMMARY

From the foregoing discussion it is evident that adsorption offers many possibilities for removal of traces of metals in aqueous media. Direct adsorption offers good possibilities for certain metals where the pH and other conditions are appropriate. Mercury, Cu, Ag and Cr are good candidates in relatively pure water. More data are certain to be forthcoming as physical chemical sewage plants using activated carbon columns are studied in more detail.

Work on the adsorption of complexes is underway and there is a good possibility of commercialization of this approach if cheap complexing agents, such as modified lignins, can be developed. This approach would be especially attractive for potable water treatment where powdered or granular activated carbon treatment facilities are already available. Oxidized carbons pose some interesting possibilities to adsorbent manufacturers for producing materials as effective as ion exchange resins. Oxidized carbons are potentially much cheaper than resins and can be subjected to very severe treatment conditions, e.g., strong oxidants, strong acids and bases, and high temperature oxidative regeneration, which might be advantageous in case of fouling. Certainly this approach should be more fully investigated for the purification of brines, sugars, organic and inorganic chemicals.

The field of impregnated or "loaded" carbons presents infinite possibilities in removing various ions or combinations of ions. If one commercial application such as the purification of desalination effluent can be reduced to practice then the stage will be set for many other applications that use the same impregnated carbon. Experts in the field of water purification can promote this development considerably by pointing out real trace metal problems that do not respond well to ion exchange or other forms of treatment. Work is going on currently at North Carolina State University under the direction of Dr. William McKean which hopefully will result in further practical applications of this technique.

In view of the ever-widening use of activated carbon in both potable and waste water treatment, the reliance on this all purpose purifier for removal of trace metals most surely will increase. A challenge is presented both to water treatment chemists and to carbon manufacturers to optimize conditions by one or more of the aforementioned techniques to achieve high removal efficiencies of trace heavy metals at reasonable cost.

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HEAVY METALS REMOVAL BY THERMAL PROCESSES

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1. Introduction

Thermal processes may be used either for the recovery of the wastewater containing dissolved heavy metals or for the recovery or concentration of the metals themselves. The two principal thermal methods are evaporation and freezing, both of which involve phase changes and the nonisothermal transfer of heat. In evaporation the wastewater is either partially or wholly vaporized, with the condensed pure vapor yielding the recovered fresh water and the non-volatile concentrate the dissolved metals. In freezing, the waste process water is partially frozen and the pure ice crystals formed are separated from the more concentrated solution and melted to yield the clean water. It should be noted that whereas evaporation is an established commercial method in heavy metal recovery and pollution control, as in the metal finishing industry, freezing (as distinct from precipitation by cooling) has not yet been developed beyond the pilot plant stage.

Among the general advantages which may be cited for thermal processes is that they can concentrate to any desired level, without incurring the severe economic penalties inherent in other methods whose energy requirements are strongly concentration dependent. By the same token such processes will generally prove economical only when applied to relatively concentrated wastewaters. Of course, the reduction of any trace contaminant for either recovery or reuse will generally involve a high concentration processing stage. Another advantage of such methods is that there are generally no chemical byproducts. Finally, they are not specific with respect to the dissolved solids, and are capable of handling wide varieties of mixed wastewaters which may be the products of the combining of various unsegregated wastes.

A principal disadvantage of thermal methods is that they tend to be energy intensive because of their nonisothermal character. This is particularly true of evaporative systems. A consequence of an inefficient thermal performance is the relative insensitivity of the economics to contaminant concentration. This results from the fact that the energy requirements are greatly in excess of the minimum thermodynamic energy to separate out the contaminant, the value of which does increase with contaminant concentration. It follows that any savings due to reduced concentrations amount to only a small reduction in the overall cost. Other basic disadvantages with evaporation are the scale and corrosion problems which are always an inherent byproduct of high temperature operation. Corrosion is particularly acute with heavy metal solutions such as chromic acid and copper, nickel and zinc acid solutions. In freezing, although scale and corrosion problems are minimized, there is a disadvantage of increased capital costs and mechanical complexity associated with the requirements of growing, handling and washing ice crystals.

Recycling of plating chemicals by evaporative recovery is a method presently in use in the metal finishing industry[1]. Chromium, cyanide and nickel plating baths are among the many solutions handled in which a wide variety of heavy metal contaminants are to be found. Shown in Fig. 1 is a simplified flow diagram of a closed loop evaporative system used to recover for reuse the chemicals lost in the "dragout" which is carried on the work from tank to tank. The only chemical addition necessary is that required to make up for the actual deposition and accidental loss[1,2]. It is to be noted that the plating solution is also circulated through the thermal process as a means of minimizing the degree of concentration required and to enable additions to the system. A similar system has been proposed using freezing as the thermal process[3]. Other applications of thermal methods are in the further concentration of the regenerant wastes from ion exchange or the concentrated effluent from an electrodialysis or reverse osmosis system. An example of concentrating a reverse osmosis effluent using both evaporation and freezing may be found in the paper by Houle[4] in this conference. Finally, there are the applications involving the reclamation to dryness of heavy metals. One such example, among many, is the recovery of zinc chloride in vulcanized fiber operations[5]. Freezing, or more properly eutectic freezing[6], may also be used, wherein the concentrate is continuously frozen until the solution is saturated with respect to the dissolved solids. By further removal of heat, ice and precipitated metal salts (mostly in hydrated form) are continuously removed from the liquid phase. If desired the precipitated salts can be brought to dryness, for example, by evaporation or vacuum freeze drying[7].

2. Evaporation[*]

As a consequence of the rapidly escalating costs of energy, one of the main problems in the application of evaporation to the removal of heavy metals from wastewaters is to reduce the system energy requirement and thereby the principal operating cost. Most evaporators use heat energy, usually in the form of steam, which condenses and gives up its latent heat of about 1,000 Btu/lb. If, as is now common in the metal finishing industry, the evaporation process is carried out in a single step, then at best, a pound of pure water is obtained for every pound of steam or 1,000 Btu of energy input. Since the heating value of fuel oil is 19,000 Btu/lb, it is clear that the amount of fuel required for a simple evaporator becomes prohibitive. In particular, for every 20 lbs of water evaporated more than 1 lb of fuel oil is needed, assuming a 100% extraction of heat from the fuel. Evidently, to be at all economical any evaporation process must require that a major part of the latent heat of condensation of the steam, which is used for vaporization, in turn be reused in a regenerative fashion.

Flash evaporation

The two principal evaporative methods are flashing and boiling[9]. In flash evaporation systems there is no boiling while the heat is being transferred to the solution, with the vaporization taking place subsequent to the heat transfer step as a result of a pressure reduction. Usually the wastewater is heated in a separate heater to a temperature just under the boiling point. The wastewater is then expanded into an evaporator to a lower pressure where part of the liquid evaporates into steam. The formation of the steam takes place within bubbles inside the liquid and the water "flashes" into steam at the liquid-vapor interface. The steam then condenses on an appropriate metallic heat transfer surface, giving up its latent heat to the feed wastewater. Such flash systems only achieve a high thermal performance when the heat is used regeneratively by putting a large number of flash stages in series, with the wastewater flowing from stage to stage at successively lower pressures. Typically, 30 to 50 stages are required for a high thermal performance necessitating multimillion gallon per day throughputs for optimum configurations. For this reason we shall not consider flash systems further in the present discussion.

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[*] In the metal finishing industry the term evaporation is also used to denote concentration of the processing solution by atmospheric wet cooling towers, wherein the solution is evaporated by contacting with air[8]. Packed bed and falling film type towers are used. In the present paper the term evaporation is reserved for the process of both vaporizing and condensing water from a solution containing non-volatile dissolved heavy metals.

Boiling

In boiling systems, boiling takes place while the heat is being transferred. For example, in a single effect submerged tube evaporator (see 1st effect, Fig. 2) steam is passed through tubes submerged in the water resulting in vaporization, with the vapor condensing inside tubes in contact with a colder environment. The thermal performance of the system can be improved by reusing regeneratively the latent heat of condensation of the steam, by placing a number of effects in series as shown in Fig. 2. In the system illustrated the vapor produced in the first effect is used as a heat source for the second effect, where it is condensed in tubes in contact with the concentrated wastewater, thereby producing additional vapor, but at a lower temperature and pressure. The process is then continued in succeeding effects. In this manner the heat released by a pound of condensing steam is reused for vaporization of another pound of water at a lower temperature, the second pound of steam releasing upon condensation the latent heat to a third pound of water, and so on. Ideally, as described, in a system of n effects one would get approximately n pounds of water evaporated per pound of steam. Thus we may express the specific heat input, that is, the heat input per pound of product water as

$$q \approx L/n \quad , \qquad (1)$$

where L is the latent heat of vaporization.

The important point to be drawn from Eq. (1) is that the thermal performance, as measured by the mass of product per unit of energy input, increases in direct proportion to the number of effects n, independently of the system heat transfer characteristics. Of course, the capital cost of the system may be expected to increase in proportion to the number of effects, to which the heat transfer area is in turn proportional. The lowest overall treatment cost is then obtained by selecting that number of effects which minimizes the energy plus capital costs.

The heat transfer area A required per unit mass of product M is given approximately by[10]

$$\frac{A}{M} \approx \frac{n\,L}{h\,\Delta T} \quad , \qquad (2)$$

where h is the overall heat transfer coefficient and ΔT the total temperature drop across the system. To reduce A/M for a given number of effects, in order to reduce the capital costs, we want the highest heat transfer coefficient and the largest temperature drop across the system. Unfortunately, the problem of extending the temperature range across the effects is restricted by the fact that the feed temperature is normally fixed, requiring that the top temperature be increased. Increasing the top temperature, however, aggravates even further the corrosion problems usually faced when dealing with heavy metal solutions such as the highly corrosive chromic acid or copper, nickel or zinc acid plating solutions. In the metal finishing industry, this is one of the principal reasons, apart from minimizing thermal decomposition of brighteners and cyanides, that evaporative systems are operated under vacuum, that is, at low boiling temperatures. In addition, the problem of carbonate or sulfate scale buildup on the heat transfer surfaces can also be a limiting factor to the top temperature, since the solubility limits generally have an inverse dependence on temperature in the boiling range. Present solutions to the problem simply involve operating at concentrations and temperatures not exceeding the solubility limits. Research on seawater distillation systems has pointed up several viable alternatives, including poisoning of the nucleation sites and circulating seed solutions to provide alternative surfaces for scale deposition.

Evidently to minimize the heat transfer surface area it is always desirable to increase the heat transfer coefficient [see Eq. (2)]. Efforts in recent years to improve heat transfer coefficients in evaporators have centered on thin-film techniques employing both rising and falling films. A notable example is the vertical tube, falling film evaporator in which the vapor condenses on the outside of vertically oriented tubes, while inside there is a thin falling film of evaporating feed[9,10]. Heat transfer coefficients have been increased even further by using tubes of fluted cross section, which result in a thinning of the film on the crests, because the liquid tends to flow from the crests to the valleys. The thin film on the convex portion of the tube is maintained by surface tension and offers little resistance to heat transfer. Heat transfer coefficients of 5,000 Btu/hr·ft^2·°F appear to be achievable with such configurations. Discussion of the various means for obtaining enhanced heat transfer coefficients, including dropwise condensation and wiped film evaporators, is beyond the scope of the present paper but should be considered when evaluating the future of evaporative systems for heavy metal removal.

Vapor compression

With energy costs now a predominant consideration in any water treatment system, renewed interest is being given to the vapor compression evaporation method[10]. This process employs mechanical energy and has a higher thermal performance than boiling systems. The principle behind the method is that the temperature driving force required for heat transfer is obtained by mechanical compression of the vapor instead of by heating. The vapor compression principle is most easily described with reference to Fig. 3, where a simplified flow diagram of a submerged tube vapor compression process is pictured. In the system illustrated, preheated feed is introduced into an evaporator say, for example, at atmospheric pressure. A portion of the feed containing the dissolved metals is then boiled by heat conducted through tubes in contact with it. The saturated vapor which is produced is compressed, thereby raising its saturation temperature. The compressed and superheated vapor passes through the tubes in contact with the feed, where it is cooled and then condensed at constant pressure releasing its latent heat to vaporize additional water. The driving temperature difference for the heat transfer is supplied by the fact that the temperature in the cooling and condensing process is greater than or equal to the saturation temperature, which because of the increased pressure is greater than the boiling point of the feed containing the dissolved solids. The terminal heat exchanger, shown enclosed by the dashed lines in Fig. 3, can be made smaller by operating the system under vacuum, although it is then necessary to handle and compress correspondingly larger vapor volumes.

The work energy input per unit mass of compressed vapor (product water) is given approximately by[11] [cf. Eq. (1)]

$$W \approx \frac{1}{\eta_c} L \frac{\Delta T}{T_{bp}} \quad , \qquad (3)$$

where ΔT includes the temperature difference required to overcome the boiling point elevation due to the presence of the dissolved solids plus the temperature difference required for heat transfer, T_{bp} is the boiling point temperature, and η_c the compressor efficiency. The corresponding heat transfer surface per unit mass of product [cf. Eq. (2)] is

$$\frac{A}{M} \approx \frac{L}{h\,\Delta T} \quad . \tag{4}$$

With a typical driving temperature difference of 10°F and a compressor efficiency of 70% it is evident from a comparison of Eqs. (1) and (3) that the energy consumption (measured in shaft work) is much smaller than that for thermal distillation. Per unit of energy input, a vapor compression system will "pump" anywhere from 5 to 10 times the latent heat that a thermal distillation system will. At present, work energy requirements of 50 kwh/1000 gallons of product water are obtainable in single effect vapor compression units for sea water desalination with outputs of about 100,000 gallons/day. This is only somewhat more than ten times the ideal theoretical minimum work energy which is required. Of course, a penalty is paid in vapor compression units in the higher capital costs associated with the compressor required to handle the large volume flows of vapor and in the higher operating costs associated with the maintenance of rotating machinery.

In the same manner as described for boiling systems, the advent of thin-film heat transfer surfaces and improved scale control techniques has reduced the heat transfer surface required. Comparison of Eqs. (4) and (2) shows that the driving temperature and heat transfer coefficient affect the area requirement similarly for both processes. Of course, in the treatment of heavy metal wastewaters the problem of carryover of corrosive volatiles and of corrosive concentrates by entrainment can make the corrosion problem a much more difficult one with vapor compression systems than with thermal distillation. However, suitable equipment and compressors are available for handling such vapors and the increased costs now appear to be outweighed by the escalating price of energy.

As with boiling systems, vapor compression units can also be staged to reduce the compressor work. Such staging may be advantageous when the concentration ratio is high and the boiling point elevation becomes large.

3. Freezing

The other thermal method applicable to heavy metal removal is freezing[9,10]. In freeze distillation two basic refrigeration systems are used to partially freeze the wastewater to produce a concentrated solution and pure ice crystals free of any contaminants. In vacuum flash freezing the water itself is the refrigerant, while in secondary refrigerant freezing a refrigerant that is immiscible with water is used. Both processes are direct contact ones in that there is no heat transfer surface interposed between the evaporating refrigerant and the process water from which the ice is frozen.

Figure 4 is a simplified flow diagram of the vacuum freezing process. Its relation to the vapor compression process just described is evident. In this system the pressure is reduced below atmospheric in a freezer to which precooled feed has been introduced, thereby causing the water to vaporize and ice crystals to form. These pure ice crystals, from which any of the dissolved metals or other contaminants have been excluded by their highly organized structure, are separated from the ice-concentrate slurry in a wash column. The separated ice is then melted by direct contact condensation of the water vapor on the ice to yield the product. The water vapor has been compressed from its lower equilibrium vapor pressure in contact with the waste solution to the higher value of pure water at its freezing point. Since the process is not ideal, auxiliary refrigeration is needed to remove the heat that enters the system because of inefficiencies, and a terminal heat exchanger is required to transfer the heat from the feed to product streams.

In the secondary refrigerant method the process description is essentially the same, except that it is an immiscible refrigerant introduced into the freezer which vaporizes at high pressures of from 1 to 5 atmospheres resulting in ice formation. The process is then as described for vacuum freezing with the refrigerant vapor compressed and put in direct contact with the ice where it condenses at the same time that the ice is melted. Because of their different specific gravities, the product water and refrigerant form stratified liquid phases which are readily separated. Typical refrigerants are one of the fluorocarbons (Freon) and n-butane. In the secondary refrigerant process described by Campbell[3,12] indirect melting is used to ensure that noncondensible volatiles will not carry over from the freezer and compromise the quality of the product.

An advantage of direct contact freezing is that the energy consumption is low in comparison with thermal evaporation. This results from the fact that the driving potentials for freezing (and melting if direct contact is used) are low because of the direct contact transfer of heat. It is expected that commercial units would, on a comparable basis, have energy consumptions less than for vapor compressor systems since the freezing heat transfer processes are direct in comparison with indirect for vapor compression. Perhaps of equal importance in the removal of heavy metals, is that problems of scaling and corrosion are much reduced in comparison with evaporation because of the low operating temperatures. The disadvantages already noted are associated with increased capital and maintenance costs associated with the requirements of growing, handling, and washing ice crystals, along with the mechanical vapor compression. Until recently, one of the main difficulties with freeze systems has been the relatively large size of the wash column and large amounts of fresh water needed to wash off the concentrated waste from the ice crystals. These limitations have now been overcome with the development of a pressurized wash column operating on the principle of one fluid displacing another within a porous medium[13,14]. In such a column, shown schematically in Fig. 5, the concentrate adhering to the ice by surface tension is displaced by fresh product water from the interstices of a porous, packed bed of the ice crystals.

The slurry of concentrated waste and ice crystals enters the bottom of the column, which is generally cylindrical, under several atmospheres pressure and at a constant rate. The ice crystals form a moving porous plug in the column, with the concentrate simultaneously flowing upward through the plug and diverging outward toward an annular screen located in the column wall about midway up its length. The pressure at the screen is held at a value below that at the bottom of the plug so that there is a "suction" effect there. At the same time, a small amount of fresh wash water is supplied to the top of the ice plug at a pressure greater than that at the screen but less than that at the bottom of the plug. The wash water filters downward through the upwardly moving plug and out toward the screen, displacing any waste in the interstices and filling up the voids in the plug above the screen. The plug itself is continuously scraped off at the top of the column along with the entrained fresh water. The result is that, in the neighborhood of the screen, there is a separation surface in the ice plug above which there is only fresh water in the voids and below which there is only concentrated waste in the voids. Of course, the pressure difference across the plug must be sufficient to drive it and the entrained fluid at the constant velocity desired.

The problem of the design of efficient freezers is still the subject of development, with efforts being centered on secondary refrigerant freezers[10]. The greater attention to secondary refrigerant freezing results from the fact that the higher operating pressures permit the use of much smaller mechanical vapor compressors, since the vapor flow volumes are from 100 to 500 times less than the water vapor volumes encountered in vacuum freezing. The problem in freezer design is to obtain a sufficiently comprehensive understanding of the nucleation and growth of ice crystals in the concentrate so that equipment can be designed with as high a rate of ice production per unit volume of freezer as possible, to reduce the capital cost. At the same time, to minimize the energy cost, the vaporization should take place at the lowest compatible driving temperature and the least expenditure of energy associated with such operations as mixing. In addition, it is also desirable to obtain the largest crystal sizes possible without significantly increasing either the capital or energy charges since, in any case, the larger the crystals the less costly will be the task of removing the concentrated waste from them.

Eutectic freezing

Recently the secondary refrigerant freezing process has been designed to carry its operation down to the eutectic point of dissolved metallic salts[6]. In this process the concentrated waste is continuously frozen, with the ice crystals precipitating out until the eutectic temperature is reached, at which point the solution is saturated with respect to the dissolved salts. The eutectic temperature for sodium chloride is $-6^{\circ}F$ and is about the same value for most inorganic salts, with very few salts having a eutectic temperature below $-10^{\circ}F$. The important point is that after the eutectic temperature is reached any further removal of heat from the system leads to crystallization of the dissolved salts, generally in a hydrated form. Continued removal of heat results both in continued ice formation and salt precipitation with no further reduction in temperature and with the concentration of the residual liquor remaining unchanged.

Laboratory experiments have shown that the ice and salts can be grown and nucleated as mechanically separate phases in a direct contact freezer; that the ice can be handled and pumped in conventional piping without freeze-up or clumping; and that the ice can be separated from the salts by means of hydrocyclones. A 5,000 gallon per day pilot plant is now installed in a mobile trailer and is presently undergoing tests, the results of which are described more fully in the paper by Campbell in this conference[12]. A major application of this process is envisaged for the treatment of plating wastes in the metal finishing industry[6]. It should be pointed out that the eutectic freeze concentration process differs from the freezing system pictured in Fig. 4, in that it is designed as a two stage process because concentration of the liquor down to the eutectic point in a single step requires considerably more compressor work than a two-stage process. The thermodynamic reasoning for such staging parallels that for additional evaporators in vapor compression units.

As we have already noted, the salts will generally crystallize out in a hydrated form, for example, sodium chloride in the dihydrate form which is 62% NaCl by weight. If it is desired to bring the hydrated metallic salt to dryness then additional evaporation is required. Bench scale experiments on the application of conventional vacuum freeze drying techniques for the recovery to dryness of heavy metals from spent plating and etching baths following freeze precipitation are described in Ref. 7.

4. Concluding Remarks

Thermal processes can play a major role in the removal and recovery of heavy metals when they are present in waste streams in strong concentrations. It is important that the removal take place before the wastes are discharged into receiving waters where the subsequently diluted metals become traces which are far more difficult to remove because of the large water volumes.

Because of rapidly increasing world energy costs, standard flash and boiling distillation systems appear less attractive at present because of their low thermal performance and correspondingly high energy consumption. Among the thermal processes with relatively low energy consumption, vapor compression distillation and freezing stand out. Vapor compression, although not a new process, has so far not been developed for the specific purpose of handling heavy metal wastewaters. Some development, pilot plant and demonstration work is required to enable the method to treat reliably the highly corrosive and scale forming waters with corrosive distillates using efficient high volume compressors and enhanced heat transfer surfaces. At this time, freezing also appears to be quite promising, particularly since it minimizes the corrosion and scale problem. However, freezing is still in an embryonic stage from a commercial viewpoint and requires much more development and testing on heavy metal wastewaters before its potential for this application can be properly evaluated.

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Figure Titles

Fig. 1. Closed loop chemical recovery system for plating and rinse operations.

Fig. 2. Submerged tube multieffect evaporator.

Fig. 3. Vapor compression evaporation.

Fig. 4. Vacuum freezing.

Fig. 5. Pressurized wash column.

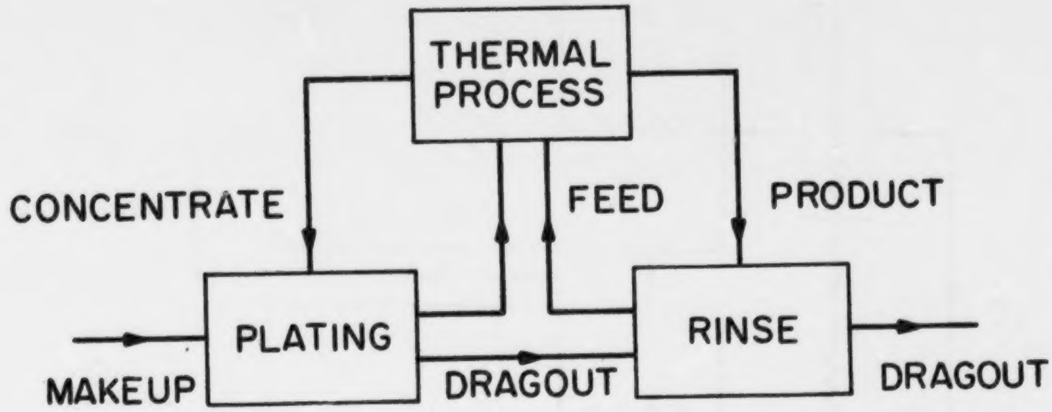
THERMAL PROCESS
CONCENTRATE
FEED
PRODUCT
PLATING
RINSE
MAKEUP
DRAGOUT
DRAGOUT

FIGURE 1

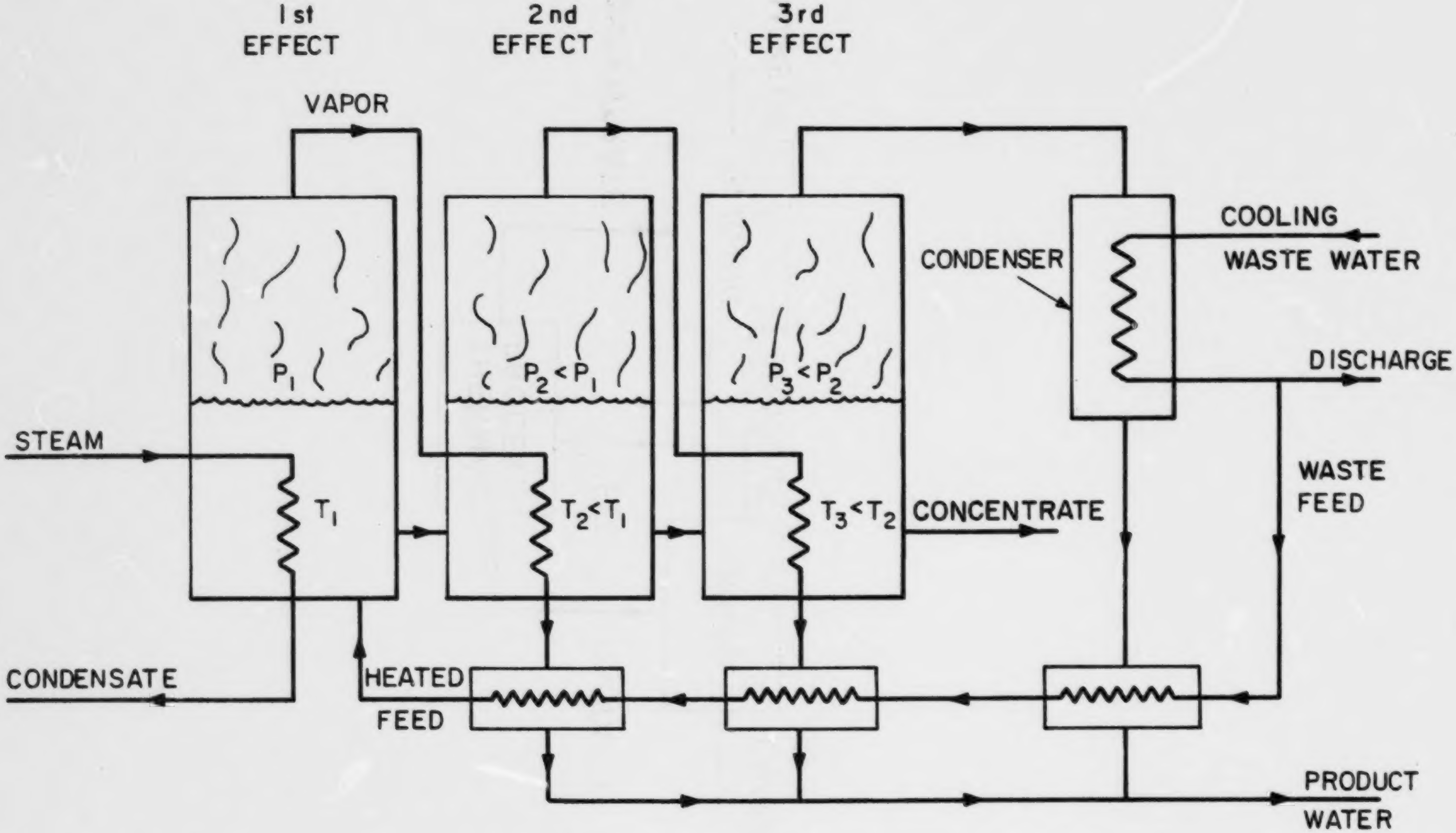
1st EFFECT
2nd EFFECT
3rd EFFECT
VAPOR
P_1
$P_2 < P_1$
$P_3 < P_2$
STEAM
T_1
$T_2 < T_1$
$T_3 < T_2$
CONCENTRATE
CONDENSER
COOLING
WASTE WATER
DISCHARGE
WASTE FEED
CONDENSATE
HEATED FEED
PRODUCT WATER

FIGURE 2

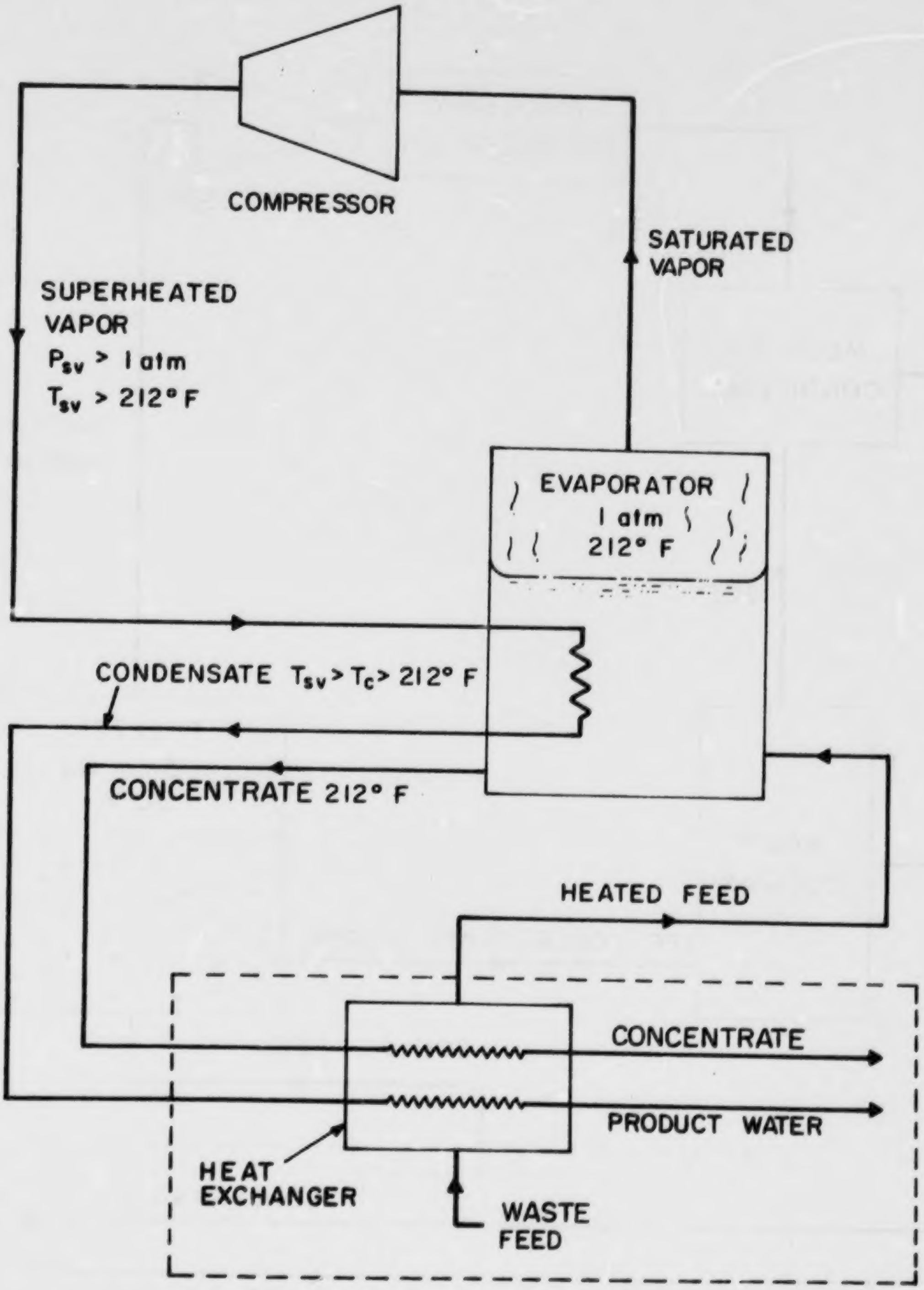
COMPRESSOR
SATURATED VAPOR
SUPERHEATED VAPOR
$P_{sv} > 1$ atm
$T_{sv} > 212°$ F
EVAPORATOR
1 atm
212° F
CONDENSATE $T_{sv} > T_c > 212°$ F
CONCENTRATE 212° F
HEATED FEED
CONCENTRATE
PRODUCT WATER
HEAT EXCHANGER
WASTE FEED

FIGURE 3

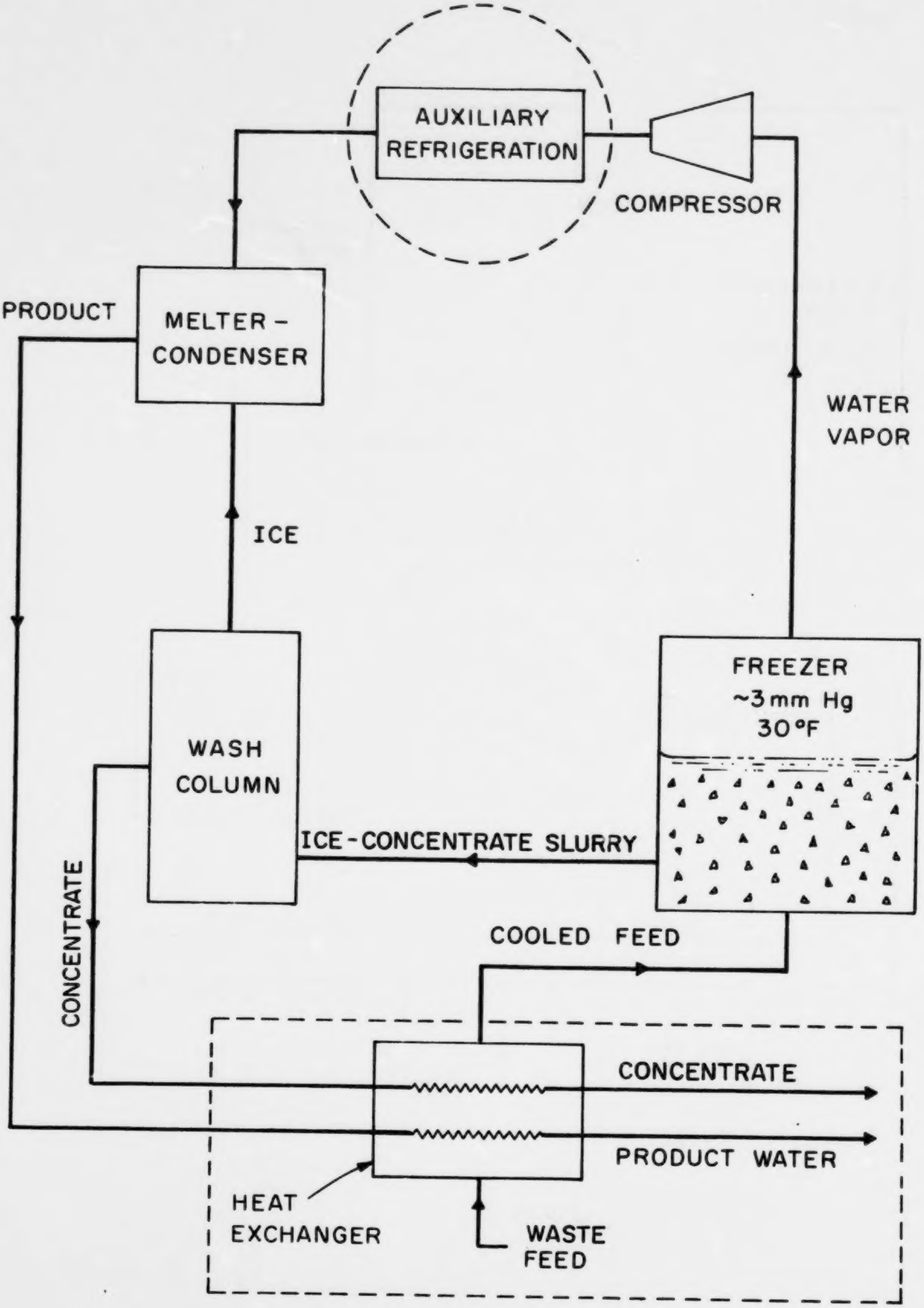
AUXILIARY REFRIGERATION
COMPRESSOR
PRODUCT
MELTER - CONDENSER
WATER VAPOR
ICE
FREEZER
~3 mm Hg
30°F
WASH COLUMN
ICE - CONCENTRATE SLURRY
CONCENTRATE
COOLED FEED
CONCENTRATE
PRODUCT WATER
HEAT EXCHANGER
WASTE FEED

FIGURE 4

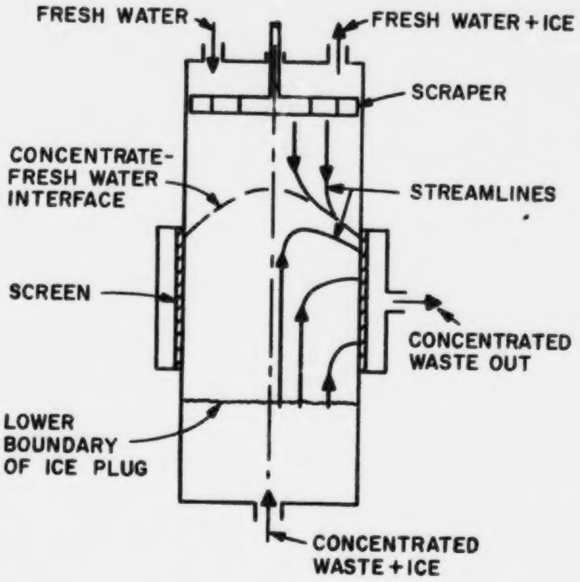
FRESH WATER
FRESH WATER + ICE
SCRAPER
CONCENTRATE-FRESH WATER INTERFACE
STREAMLINES
SCREEN
CONCENTRATED WASTE OUT
LOWER BOUNDARY OF ICE PLUG
CONCENTRATED WASTE + ICE

FIGURE 5

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Princeton University Center for Environmental Studies
Environmental Protection Agency
American Institute of Chemical Engineers

Conference on

"Traces of Heavy Metals in Water: Removal Processes and Monitoring"

November 15 and 16, 1973

FREEZING CONCENTRATION FOR REMOVAL OF HEAVY METALS FROM WATER

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Freezing Concentration for Removal of Heavy Metals from Water

Traces of heavy metals occur in waters which have been used in processes wherein they are an integral part of the process, or in cases where the water may be in contact with metallic materials containing heavy metal elements. The alternatives facing the owner of the contaminated water are: (1) remove the heavy metals to the degree required to permit discharge of the water from his site or (2) remove the heavy metals and other constituents from the waste stream to the extent necessary to permit re-use of the water within his plant. By removing all of the contaminants from the water in equal proportions, the freezing process permits reuse of the contaminated water within the plant.

The application of the freezing process to treatment and reuse of waste water results directly in the removal of heavy metals which may exist only in trace quantities. The contaminant is concentrated in a much smaller volume which may then be re-used or disposed of as appropriate. While reductions in heavy metal concentrations achieved by freezing may in many cases result in conformance with discharge standards, the maximum benefit is derived by recycling the treated water to the process. In this way the monitoring and reporting of discharges is not required, and the cost of purchasing and eventual sewering of water is eliminated. In some cases, valuable chemicals can also be recovered.

The CRYSTALEX^{tm} freezing process developed by Avco removes pure water from aqueous solutions of various contaminants. It is only slightly sensitive to the type of contaminant in that high concentrations lower the freezing point of the solution. Corrosion of equipment is substantially reduced at the low operating temperatures characteristic of the process. Plant size and operating costs are functions of the quantities of water treated, and economy in the use of water is an important part of any overall treatment system. Countercurrent rinsing of plated parts or circuit boards is typical of such measures.

The process is not selective with respect to rejection of specific dissolved contaminants. All are reduced to the same degree in the product and are concentrated in the brine. However, in some cases, one or more of the contaminants may precipitate from solution, either as a result of solubility reductions at low temperatures, or due to increased concentrations of the solutions. The precipitate is then filtered from the process for disposal or recycle as appropriate. Final disposal of the concentrate depends on several factors. Concentrates from treatment of plating rinses may frequently be returned to the plating bath, since they may contain valuable chemicals and they constitute the dragout from the bath. The vastly reduced quantity of water involved may make incineration or drying of concentrates an attractive solution. Chemical treatment and disposal of highly concentrated wastes may be the best solution in other cases. The high concentration and the much smaller quantities of water involved make possible disposal solutions which would otherwise be impractical.

Process Capabilities

The capabilities of the freezing process are best defined in terms of purity of the recovered water, concentration of the waste, plant capacity, power consumption and applicability to various streams. The process is applied to the concentration of aqueous solutions having freezing points as low as the eutectic point of sodium chloride (-6°F) although lower temperatures can be achieved if justified by the economics. The more usual applications are to solutions having freezing points at the brine concentration in the range of 20 to 32 degrees fahrenheit. Typical but not exclusive ranges of applications are shown in Table I.

Table I - Applications of the Crystalex Freezing Concentration Process

FEEDS

Aqueous Solutions (Rinse Waters, Process Streams, Plant Wastes) containing salts, chemicals, dissolved liquids, organic and inorganic acids. Also applicable to certain nonaqueous process streams where crystallization provides a positive process benefit.

CONCENTRATIONS

Limited only by freezing point depressions (20°F typical) and concentrate viscosity

Precipitating contaminants are separated where required.

WATER QUALITY

$$\frac{\text{Concentration in Product Water}}{\text{Concentration in Brine Solution}} = .0005 \text{ to } 0.005$$

OPERATING EXPENSES

- Electrical Power at 25°F Freezing Point

  40 KWH/1000 Gallons (100,000 GPD Plants)
  to
  75 KWH/1,000 Gallons (5000 GPD Plants)

  Note: Energy consumption based on power generation at 10,000 btu/KWH Heat Rate:
  40 KWH/1000 Gallons = 400,000 Btu/1000 gallons 100 K GPD Plant
  75 KWH/1,000 Gallons = 750,000 Btu/1000 gallons 5 K GPD Plant
  Single Effect Evaporator 8,500,000 Btu/1000 gallons
  Three Effect Evaporator 2,900,000 Btu/1000 gallons
  Six Effect Evaporator 1,500,000 Btu/1000 gallons

- Cooling Water as required to dissipate electrical power.

- Refrigerant make-up $0.01 to $0.10 per 1000 gallons depending on plant size.

- Plant is designed to operate unattended.

PLANT SIZES

Factory assembled and tested units from 5000 to 100,000 gallons per day. Multiple units may be used for larger requirements. Very large plants may be constructed on site where applications warrant.

Concentration by Freezing

Separation of contaminants and concentrated salts from water by evaporative concentration is well understood. The water phase is changed from liquid to vapor so that it may be recovered in pure form. In an analogous manner water which has been changed to the crystalline phase, ice, may also be recovered as pure water.

The essential factor in recovery of pure water by freezing is that the ice crystal, as it freezes, excludes dissolved impurities, including organics, inorganics, and volatiles; the resulting crystals consisting of pure water. If the brine which adheres to the crystals is removed, then the water resulting when the crystals are melted will be pure. The insensitivity of the process to the nature of the contaminants results in an almost universal applicability in the concentration of solutions containing dissolved contaminants. As the water is removed, the waste is concentrated. The concentration can be carried to the point of saturation where the salts precipitate out of solution. The precipitated salts can then be dried for disposal or convenient transportation to a recycling center.

The feed, consisting of contaminated water, is pumped into the system through a heat exchanger, where it is cooled by heat exchange with the purified water from the melted ice (Figure 1). The cold feed enters the freezer where it is mixed with an immiscible refrigerant. The evaporation of the refrigerant removes heat from the feed water forming a slurry consisting of ice and the concentrated brine. The refrigerant vapor is pumped out of the freezer with a compressor. The slurry is pumped from the freezer to a counterwasher where the adhered brine is washed from the ice crystals.

The counterwasher is a simple vertical vessel with screened outlet located midway between top and bottom. The slurry enters the bottom and forms a porous plug, the majority of the brine flowing upward through the plug and leaving the counterwasher through the screen. The ice plug is propelled through the column by the force resulting from the pressure drop of the brine flowing through the ice plug, the velocity of the brine being much greater than that of ice. Fresh water from the previously produced product is circulated at top of the ice plug, and a small fraction of the product (less than five percent) flows countercurrently to the ice plug, washing away the adhered brine.

The ice is removed from the top of the counterwasher where it is reslurried with previously produced product. The slurry is pumped to a condenser where the ice is melted by the release of heat from the condensing refrigerant vapor which was evaporated to produce the ice, and which has been heated by compression to a saturation temperature higher than the melting point of the ice.

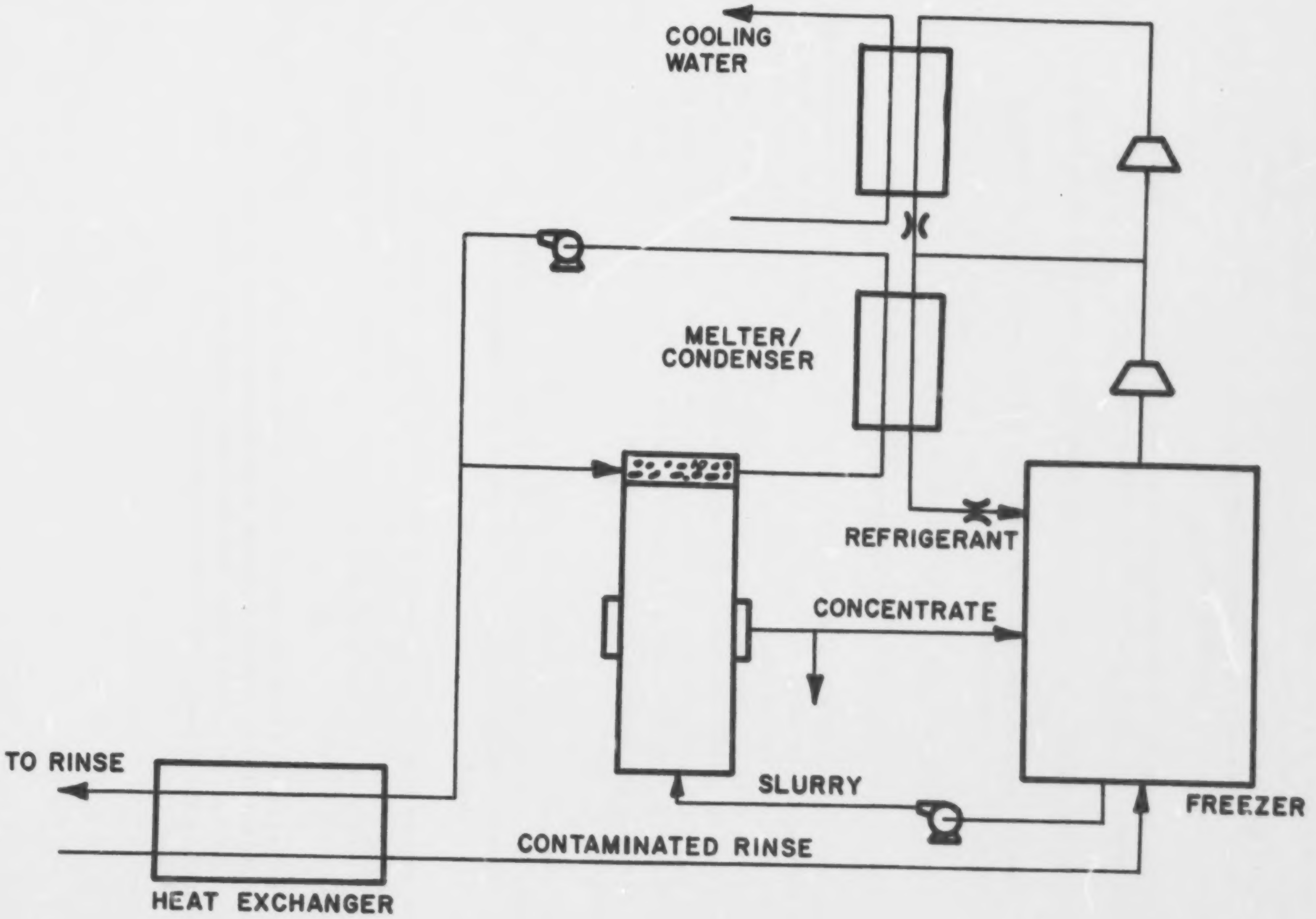
COOLING WATER
MELTER/ CONDENSER
REFRIGERANT
CONCENTRATE
SLURRY
FREEZER
TO RINSE
CONTAMINATED RINSE
HEAT EXCHANGER

Figure 1 SCHEMATIC DIAGRAM OF FREEZING PROCESS CONCENTRATION AND RECOVERY SYSTEM

Because of pump work, compressor work, and incomplete heat exchange a greater amount of refrigerant is vaporized than can be condensed by melting of the ice. A heat removal system is therefore required to maintain thermal equilibrium. This consists of a compressor which raises the excess vapor to a temperature and pressure that will cause it to condense on ambient cooling water.

From the foregoing description it can be seen that a freezing process offers several advantages for waste treatment.

1. Concentration is performed in the absence of a surface of membrane.

2. The process operates at temperatures below ambient, minimizing corrosion of materials.

3. The process has low energy requirements.

4. There is no carryover of volatiles to the product.

Since concentration takes place by freezing out of water in direct contact with the refrigerant there is no heat transfer surface or membrane to be fouled by the concentrate or other contaminants. Therefore, feed pre-treatment to prevent such scaling or other fouling is unnecessary even with waters that present severe problems with other processes. Where heat exchange surfaces are used they are not associated with concentration of the fluids and therefore deposits are minimized. Suspended solids do not affect the process and are removed only as required by the end use of the recovered products.

Low temperature operation of the process minimizes corrosion and also allows the use of non-metallic corrosion resistant materials for piping, pumps and vessels. Much of the cost associated with evaporation processes is thus eliminated.

Low energy requirements reduce operating costs and result in a drastic reduction of cooling water requirements compared to evaporators. The low cost holds even though electrical power is used, and steam generating equipment is not required.

One impediment to the re-use of water recovered from evaporative systems is the fact that it may contain volatile contaminants which were present in the feed. In the freezing process volatiles are isolated from the washed product by the tubes of the melter/condenser.

Application Testing

A solution containing approximately 100 milligrams per liter of nickel, cadmium, chromium, and zinc was tested in a 2500 gallon per day pilot plant. The recovered water contained less than 0.5 milligram per liter (see Table 2), yielding removal of more than 99.5 percent of the contaminant. The purity of the final product is controlled by the length of the washing zone in the counterwasher, and to some extent by the quantity of wash water used. Extremely low concentrations may be achieved where required.

A 5000 gallon per day mobile pilot plant has also been built and at this time is being used to treat wastes containing heavy metals as well as large quantities of various dissolved salts which are removed by concentration and precipitation.

TABLE 2

METAL ION SEPARATION TEST RESULTS

Element	Concentration In Feed mg/liter	Concentration In Product mg/liter	Percent Removed
Nickel	105	0.44	99.58
Cadmium	105	0.40	99.62
Chromium	110	0.225	99.80
Zinc	100	0.34	99.66
NaCl	30.000	120.	99.60

Acknowledgements

The processes described are currently being developed by the Systems Division of Avco Corporation in Wilmington, Massachusetts. The waste treatment application is an extension of a desalination process being developed by Avco with the cooperation and support of the Office of Saline Water of the United States Department of the Interior.

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More detailed discussions of the freeze crystallization process and descriptions of applications are found in the following references.

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MEMBRANE PROCESSES FOR WASTE TREATMENT

A Paper for the Princeton University Center for Environmental Studies Conference on Removal of Heavy Metals from Waste Water, November 15-16, 1973.

by

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MEMBRANE PROCESSES FOR WASTE TREATMENT

A Paper for the Princeton University Center for Environmental Studies Conference on Removal of Heavy Metals from Waste Water, November 15-16, 1973.

Membrane processes, such as electrodialysis and reverse osmosis, have promise for use in removing heavy metals from wastewater, and specific applications of membrane processes for the treatment of wastewaters are discussed in the papers that follow this presentation. In this paper the status and basic principles of electrodialysis and reverse osmosis are given to provide background information for the papers that follow.

I. ELECTRODIALYSIS

Electrodialysis is the transport of ions through membranes as a result of an electrical driving force. It is the underlying principle of all electrically driven membrane processes. When nonselective membranes that are permeable to ions (*e.g.*, cellophane) are used, electrolytes can be separated from nonelectrolytes. When membranes that are more permeable to cations than anions or *vice versa* (*e.g.*, ion-exchange membranes) are used, concentrations of electrolytes in solutions can be increased or decreased. Thus, electrodialysis can accomplish practical concentration or depletion of electrolytes in solution as well as the separation of electrolytes from nonelectrolytes. Excellent reviews in the recent literature[1-3] describe the historical development of electrodialysis, so no discussion of history is presented here.

In any membrane process the selective membrane is the heart of the process. Therefore, a discussion of the nature of the selective membranes used in electrodialysis is presented first.

A. Ion-Exchange Membranes

Ion-exchange membranes are used in most electrodialytic processes. They are ion exchangers in the form of films. There are two basic types: cation-exchange and anion-exchange membranes. Ion-exchange membranes are selective in that they are permeable to cations, but not to anions, or *vice versa*. In Figure 1, polymer chains are shown that have negatively charged groups chemically attached to them. The polymer chains are intertwined and also crosslinked at various points. Positive ions are shown

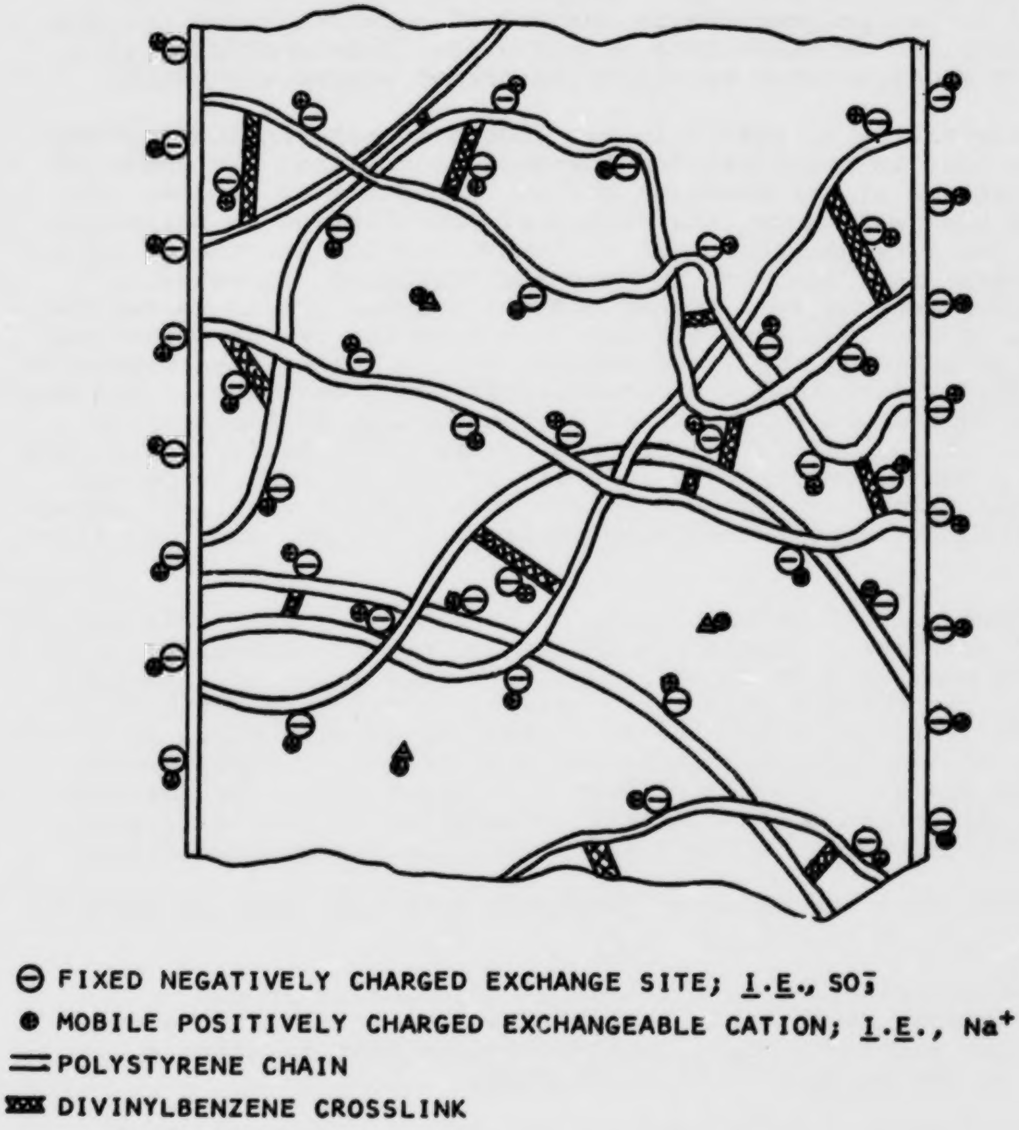

⊖ FIXED NEGATIVELY CHARGED EXCHANGE SITE; I.E., SO_3^-
● MOBILE POSITIVELY CHARGED EXCHANGEABLE CATION; I.E., Na^+
═ POLYSTYRENE CHAIN
▨ DIVINYLBENZENE CROSSLINK

Figure 1. Representation of an Ion-Exchange Membrane

freely dispersed in the voids between the chains. However, the fixed negative charges on the chains repel negative ions that try to enter the membrane, and exclude them. Thus, because of the negative fixed charges, negative ions cannot permeate the membrane, but positive ones can. If positive fixed charges are attached to the polymer chains instead of negative fixed charges, selectivity for negative ions is achieved. This exclusion as a result of electrostatic repulsion is termed Donnan exclusion.

Selectivity by itself is not enough to make an ion-exchange membrane that is practical for low-cost processing. In addition, the resistance of the membrane to ion transfer must be low. To decrease the resistance, the degree of crosslinking is decreased so that the average interchain distances and the lengths of polymer segments that are free to move are increased. However, if this enlargement of void spaces between polymer chains is carried too far, it can result in volumes in the center of the voids that are not affected by the fixed charges on the chains (the repulsion effect of fixed charges decreases rapidly with distance). Volumes that are unaffected by the fixed charges result in ineffective repulsion of the undesired ions and lowered selectivity. For this reason, a compromise between selectivity and low resistance must usually be made. Membranes now available combine excellent selectivity with low resistance, high physical strength, and long lifetimes.

There are two general types of commercially available ion-exchange membranes: heterogenous and homogenous membranes. Heterogenous membranes in which ion-exchange particles are incorporated in film-forming resins are made by calendering mixtures of ion-exchange and film-forming materials, by casting films from dispersions of ion-exchange materials in solutions of film-forming materials and allowing the solvent to evaporate, and by casting films of dispersions of ion-exchange material in partially polymerized film-forming polymers and completing the polymerization.

Homogenous ion-exchange membranes have been made by several methods:

—Polymerization of mixtures of reactants that can undergo condensation polymerization. At least one of the reactants must contain a moiety that is anionic or can be made to be so charged.

—Polymerization of mixtures of reactants (one of which is anionic or cationic) that can undergo additional polymerization.

—Graft polymerization of moieties that are anionic or cationic (or can be made to be) into preformed films.

—Casting films from a solution of a linear film-forming polymer and a linear polyelectrolyte, and allowing the solvent to evaporate.

B. Concentration and Depletion by Electrodialysis

In an electrodialysis stack used for concentration or depletion of electrolytes in solution, cation-exchange membranes alternate with anion-exchange membranes in a parallel array to form thin solution-compartments (0.5 to 1.0 mm thick). The entire assembly of membranes is held between two electrodes as shown in Figure 2. A solution to be treated is circulated through the solution compartments. With the application of an electrical potential to the electrodes, all cations tend to transfer toward the cathode and all anions tend to move toward the anode. The ions in the even-numbered compartments transfer through the first membranes they encounter (cations through cation-exchange membranes, anions through anion-exchange membranes), but they are blocked by the next membranes they encounter as indicated by the arrows in the diagram. Ions in the odd-numbered compartments are blocked in both directions. By this mechanism, ions are removed from the solution circulating through one set of compartments (even) and transferred to the other set of compartments (odd). Ion depletion is accomplished for one solution, and ion concentration is accomplished for the second solution.

An electrodialysis stack is essentially a device to hold an array of membranes parallel to each other between electrodes in such a way that the solutions being processed are kept separated.

Figure 3 is an exploded view of part of an electromembrane stack that shows the main components. Component 1 in Figure 3 is one of the two end frames, each of which has provisions for holding an electrode and introducing and withdrawing the depleting, the concentrating, and the electrode-rinse solutions. The end frames are made relatively thick and rigid so that pressure can be applied easily to hold the stack components together. The inside surfaces of the electrodes are recessed, as shown, to form an electrode-rinse compartment when an ion-exchange membrane, component 2, is clamped in place. Components 3 and 5 are spacer frames. Spacer frames have gaskets at the edges and ends so that solution compartments are formed when ion-exchange membranes and spacer frames are clamped together.

Usually the supply ducts for the various solutions are formed by matching holes in the spacer frames, membranes, gaskets, and end frames. Each spacer frame is provided with solution channels (E in Figure 3) that connect the solution-supply ducts with the solution compartments. The spacer frames have mesh spacers, or some other device, in the compartment space to support the ion-exchange membranes to prevent collapse when there is a differential pressure between two compartments.

An electromembrane stack usually has many repeated sections, each consisting of components 2, 3, 4, and 5, with a second end frame at the end.

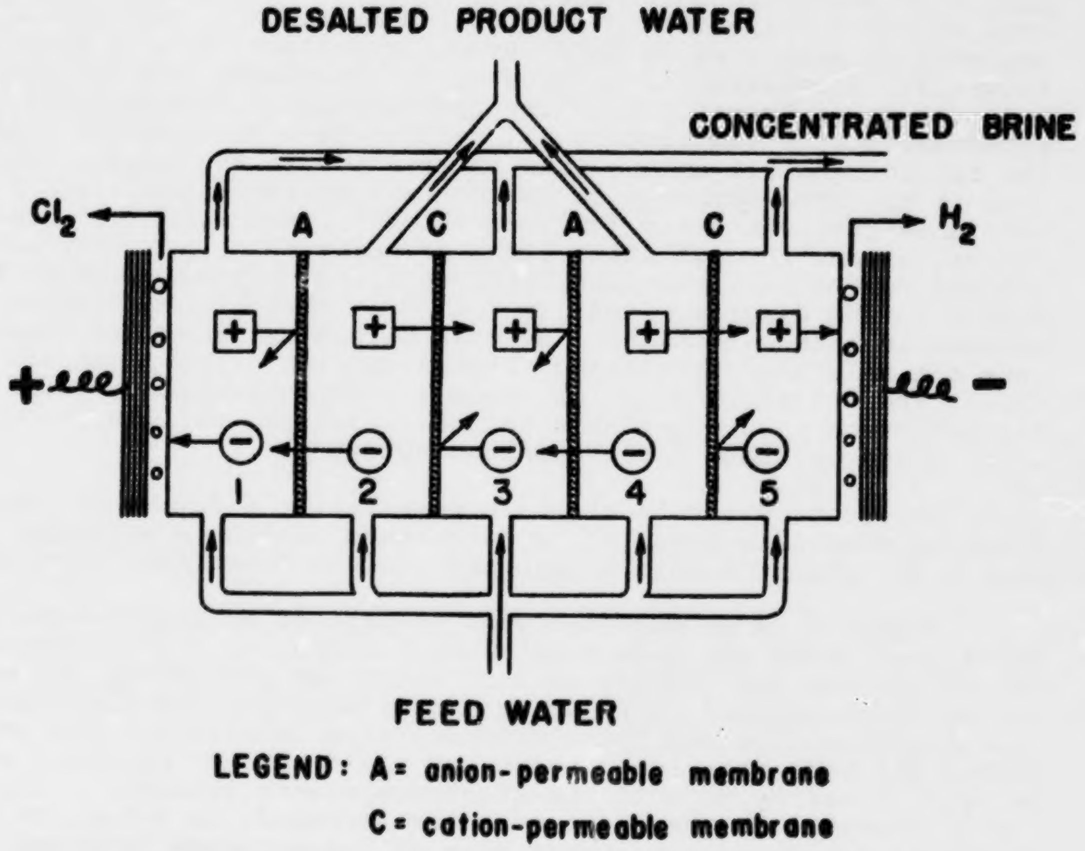

DESALTED PRODUCT WATER
CONCENTRATED BRINE
Cl_2
A
C
A
C
H_2
+
−
1
2
3
4
5
FEED WATER
LEGEND: A = anion-permeable membrane
C = cation-permeable membrane

Figure 2. Diagram of Electrodialysis Process

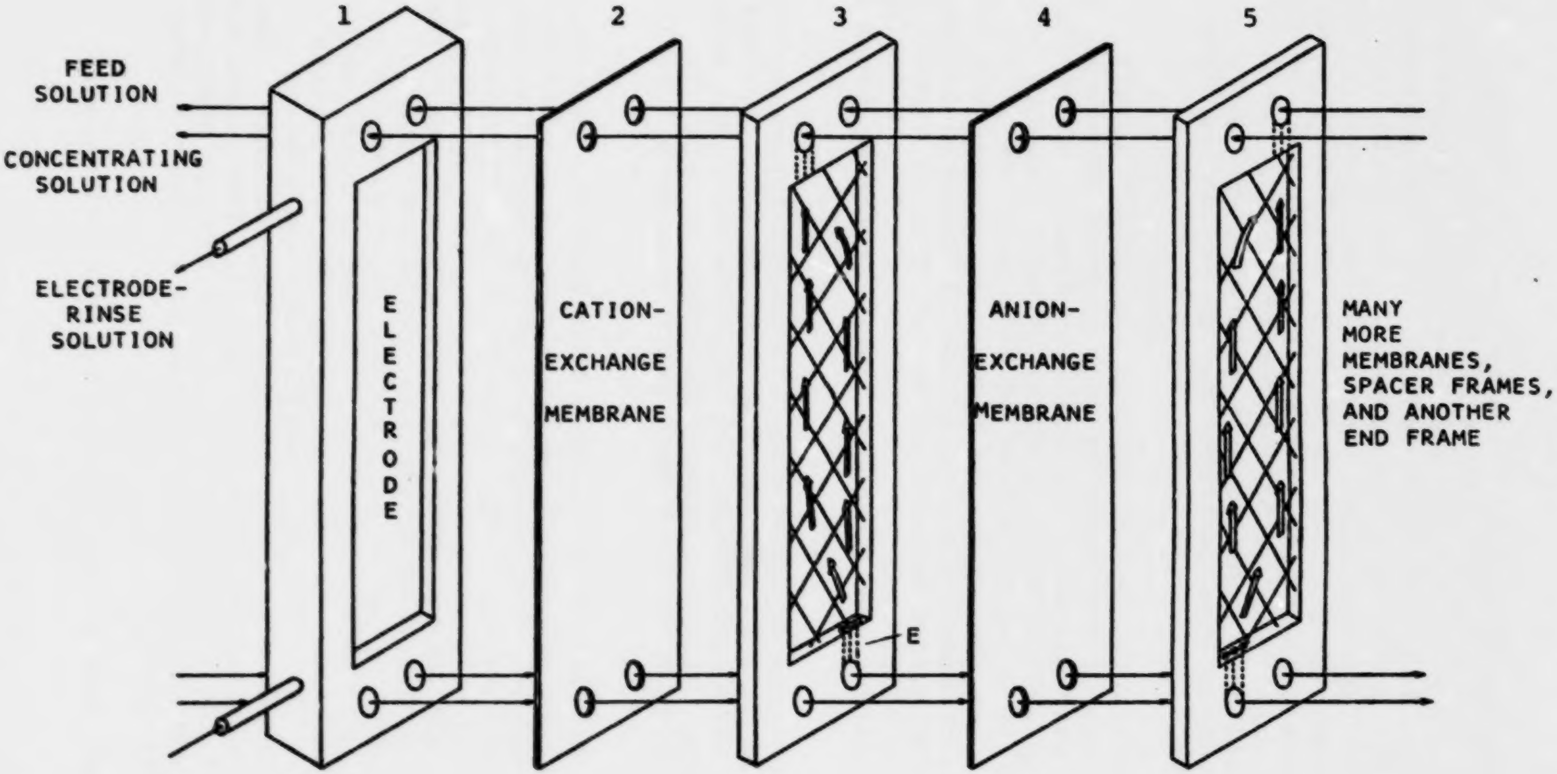

1
2
3
4
5
FEED SOLUTION
CONCENTRATING SOLUTION
ELECTRODE-RINSE SOLUTION
ELECTRODE
CATION-EXCHANGE MEMBRANE
E
ANION-EXCHANGE MEMBRANE
MANY MORE MEMBRANES, SPACER FRAMES, AND ANOTHER END FRAME

Figure 3. Main Components of an Electrodialysis Stack

There are three basic types of electrodialysis stacks: tortuous path, sheet-flow, and unit-cell stacks. In the tortuous-path stack, the solution flow path is a long narrow channel as illustrated in Figure 4, which makes several 180° bends between the entrance and exit ports of a compartment. The bottom half of the spacer gasket in Figure 4 shows the individual narrow solution channels and the cross-straps used to promote turbulence, whereas the individual channels have been omitted in the top half of the figure so the flow path could be better depicted. The ratio of channel length to width is high, usually greater than 100:1. Spacer screens to support the membranes may or may not be used in tortuous-path stacks.

In sheet-flow stacks, spacer screens are almost always needed since the width of membranes is much greater than that in the usual tortuous-path stacks. The solution flow in sheet-flow stacks is usually in approximately a straight path from one or more entrance ports to an equal number of exit ports as illustrated in Figure 3. As the solutions flow in and around the filaments of the spacer screens, a mixing action is imparted to the solutions. Thus, the spacer screens serve not only to support the membranes but to aid in mixing the solutions and in reducing the thicknesses of diffusional boundary layers at the surfaces of the membranes.

Solution velocities in sheet-flow stacks are typically in the range of 5 to 15 cm/sec, whereas the velocities in tortuous-path stacks are usually much higher, 30 to 50 cm/sec. The drop in hydraulic pressure through a sheet-flow stack is normally lower than that through a tortuous-path stack because of the lower velocities.

Unit-cell stacks were specifically developed for concentrating solutions. Each concentrating cell consists of one cation-exchange membrane and one anion-exchange membrane sealed at the edges to form an envelope-like bag. Many of these concentrate cells are assembled with spacer screens between them to separate the cells so solutions concentrated can flow between them. The entire assembly of alternating concentrate cells and spacer screens is held between a set of electrodes. When electric current flows through the stack, ions flow from the external solutions through the membranes to the insides of the concentrate cells where they are trapped. Only osmotically and electro-osmotically transferred water flows through the membranes. Thus, the maximum degree of concentration is effected. The concentrated solutions inside of the concentrate cells flow through small tubes that lead from inside the concentrate cells to a plenum chamber arranged outside the stack.

Figure 5 shows some of the details of unit-cell stacks.

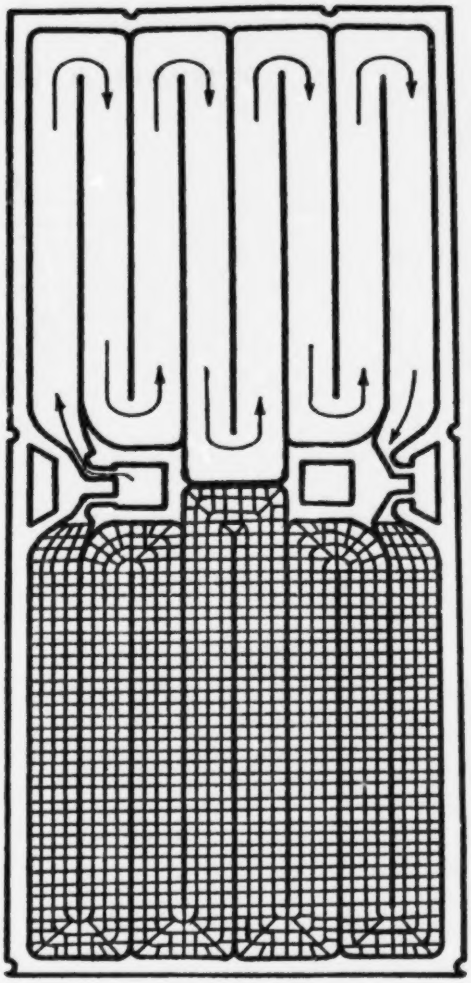


Figure 4. Diagram of a Tortuous-Path Spacer for an Electrodialysis Stack

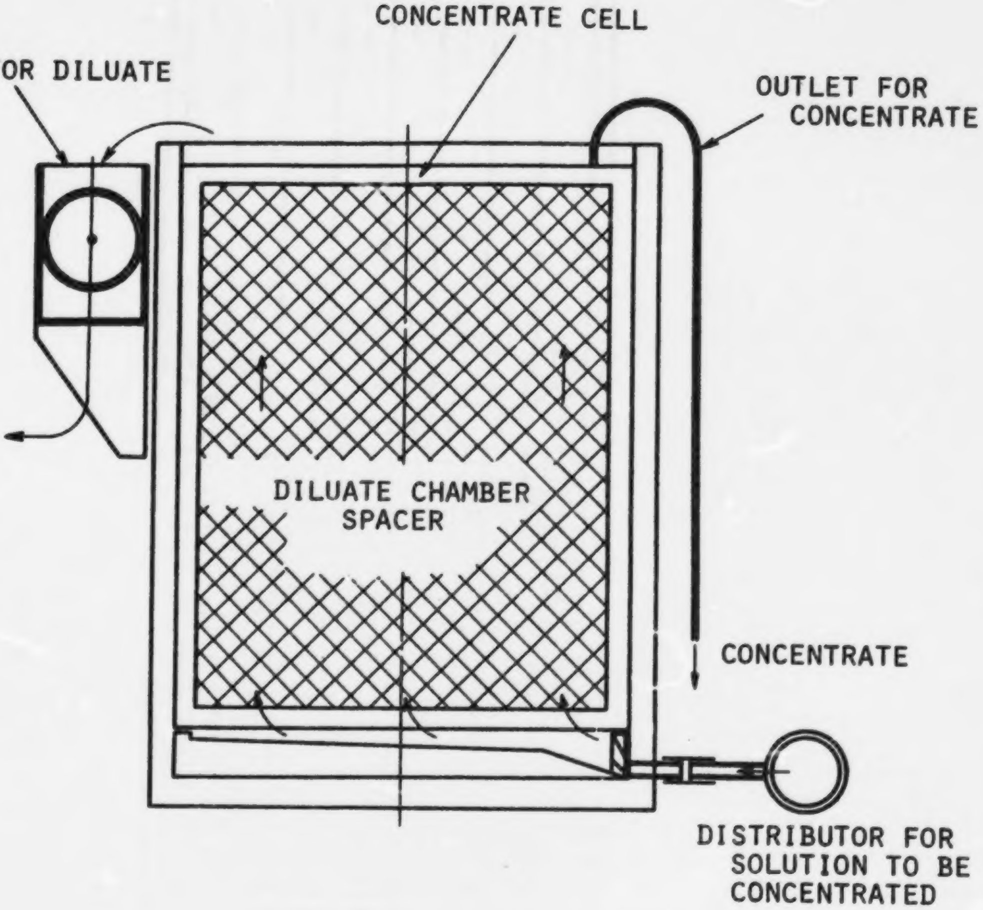
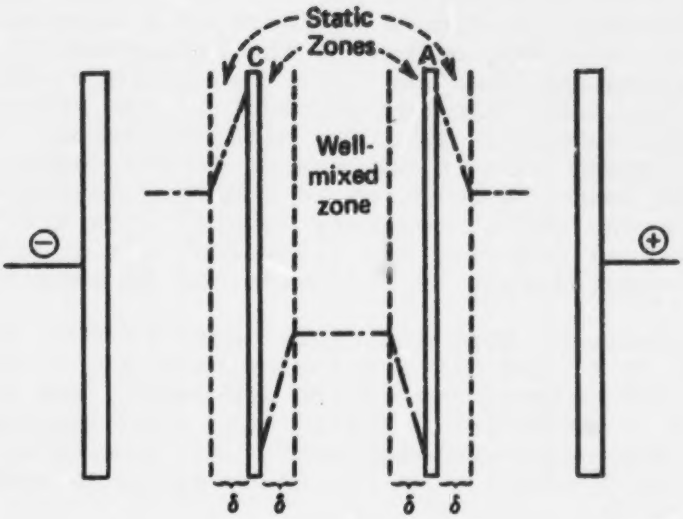

CONCENTRATE CELL
OUTLET FOR DILUATE
OUTLET FOR CONCENTRATE
DILUATE CHAMBER SPACER
CONCENTRATE
DISTRIBUTOR FOR SOLUTION TO BE CONCENTRATED

Figure 5. Main Structure of the Unit-Cell Type Electrodialysis stack


Static
Zones
C
A
Well-
mixed
zone
⊖
⊕
δ
δ
δ
δ

δ = Static boundary-layers
C = Cation-exchange membrane
A = Anion-exchange membrane

Figure 6. Concentration Gradients in Electrodialysis

C. Concentration Changes at Membrane Surfaces

The diagram in Figure 2 shows a simplified picture of the net effects of electrical current in electrodialysis stacks, but more complex changes in concentration actually occur, as indicated on an idealized basis in Figure 6.

Figure 6 shows a cation- and an anion-exchange membrane mounted between two electrodes. A solution of an electrolyte flows through the compartments formed by the two membranes. With the passage of an electrical current through the system of the membranes and solutions, anions transfer toward the cathode.

Because of the flow of solution through the center compartment formed by the two membranes in Figure 6, there is a zone of relatively well-mixed solution near the center of the compartment. The velocity of the solution and thus the degree of mixing diminish as the surfaces of the membranes are approached. In the figure, the so-called Nernst idealization is used for simplification. This assumes a completely mixed zone in the center of the compartment, and completely static zones of solution in boundary layers adjacent to the membranes. In the static boundary layers, ions are transferred only by electrical transfer and diffusion, but in the mixed zone, ions transfer electrically by diffusion and by physical mixing.

Assume for convenience that the electrolyte is KCl, since the transference numbers of K^+ and Cl^- are approximately 0.50 in solution. However, because of the selectivity of the membranes, the transference number of K^+ is essentially 1.0 in the cation-exchange membrane and 0.0 in the anion-exchange membrane. Similarly, the transference number of Cl^- is 1.0 in the anion-exchange membrane.

Consider for now only the anion-exchange membrane and its boundary layers. The Cl^- ions carry only 50% of the electrical current in solution but 100% of the current in the membrane. If 1 faraday of electricty were passed through the membrane and boundary layers, 0.5 g eq of Cl^- sould be transferred to or away from the membrane surface, and 1.0 g eq of Cl^- would be transferred through the membrane by electrical transfer. There would be a depletion of ions at the left-hand surface of the anion-exchange membrane in Figure 6 and a concentrations of ions at the right-hand surface. Obviously, this transient state of affairs could not continue long before all ions were depleted at the left surface. In steady-state operation, concentration gradients are established in the static boundary layers, as indicated by the dashed lines in Figure 6, so that the ions that are not electrically transferred to or from the membrane surface are supplied by diffusion through the boundary layers. These differences in transference numbers between solutions and membranes are the source of the depletion and concentration that occurs in electrodialysis, but they can also be a source of trouble.

If the current density is increased through the system of membranes and solutions in Figure 6, the rate of electrical transport increases. Therefore, the rate of diffusional transport must also increase to supply the extra ions needed at the surfaces of the membranes. Diffusional transport can increase if the thicknesses of the boundary layers decrease, or if the differences in concentration at the edges of the boundary layers increase. If the solution velocity past the membranes stays constant, the thicknesses of the boundary layers also remain constant and the concentration gradients increase. The interfacial concentrations on the depleting sides of the membranes decrease; those on the concentrating sides increase.

If the current density is increased still more, a density will be reached at which the concentrations of electrolytes at the membrane interfaces on the depleting sides will approach zero. At this density, usually called the limiting current density, H^+ and OH^- ions from ionization of water will be transferred through the membranes. The transfer of H^+ ions through the cation-exchange membranes is usually not particularly harmful, but transfer of OH^- ions through the anion-exchange membranes can cause increases in pH in the concentrating compartments that cause pH-sensitive substances like $CaCO_3$ or $Mg(OH)_2$ to precipitate in and on the membranes. In addition, the OH^- ions can cause dimensional changes in the anion-exchange membranes. Also, the presence of the layers of almost pure water at the membrane surfaces causes the resistance of the membrane cells to be high, and the energy requirements of the process to be high.

The thicknesses of the boundary layers decrease with increasing solution velocity. Therefore, it is important to use the highest practicable velocities, to have equal velocities in each solution compartment, and to have uniform velocities at all points along the membrane surfaces (i.e., have no points of solution stagnation).

A mathematical expression has been developed[4,5] that relates the limiting current density to the boundary-layer thickness, the concentration of electrolyte in the well-mixed zone between boundary layers, and the transference numbers of counter-ions in the membranes and solutions. This expression is based on the Nernst idealization of boundary layers. A model based on the Nernst idealization is an extremely simplified model of the actual boundary layers in electrodialysis and a number of workers have dealt with models that more nearly resemble actual boundary layers[6-8] and with hydrodynamic analyses of boundary layers.[9,10]

Despite the simple model provided by the Nernst idealization, or perhaps because of it, the mathematical expression given below is easy to use and predicts performance adequately for most design uses.

$$\frac{i_{lim}}{C_b} = \frac{DF}{\delta(\bar{t}^- - t^-)}$$

This ratio (usually written as i/N instead of i_{lim}/C_b) is often called the "polarization parameter" and is used as a design parameter in electrodialysis. Values of i/N have been found to vary with solution velocity and also with the nature and shape of the mesh-like screens or other devices used to maintain desired spacings between the ion-exchange membranes.

D. Consequences of Operation at or Above Limiting Current Density

There are three main consequences of operating at or above the limiting current density. They are: scaling of anion-exchange membranes by electrolytes that become insoluble at high values of pH, excessively high resistances of stacks, and fouling of membranes by organic ions. All three are deleterious to the performance of electrodialysis stacks.

Scaling of membranes by pH-sensitive electrolytes occurs because OH^- ions transfer through anion-exchange membranes when the limiting current density is reached. The OH^- ions increase the pH within the membrane and at the interface on the concentrating side so that substances such as $CaCO_3$ precipitate.

A second undesirable consequence of exceeding the limiting current density is increased stack resistance. When the limiting current density is reached or exceeded, the rate of dissociation of water is increased because the H^+ and OH^- ions are continuously transferred away from the membrane interfaces, which are the locations of dissociation. An increased voltage is necessary to induce this more rapid dissociation of water. Also, a thin film of highly depleted solution forms at the depleting sides of membranes. These films have extremely high specific resistances, and the high resistances are in series with the normal resistances in an electrodialysis stack. Thus, operation at or above the limiting current density causes the stack to have resistances much higher than normal.

Organic fouling may occur on either the cation- or anion-exchange membranes. However, most of the trouble that has been encountered has been fouling of anion-exchange membranes. Fouling of anion-exchange membranes has been shown to be caused by large organic ions becoming attached to charged groups on membranes having the opposite charge. Since negatively charged organic substances occur more often in natural waters than positively charged ones, anion-exchange membranes with their positive charges are fouled more often than cation-exchange membranes. Fouling of membranes by organic matter has been studied by Cooke,[11] Holting,[12] Olie,[13] Solt,[14] Mandersloot,[15] Small and Gardiner,[16] and Korngold and De Korosy.[17]

The studies of the last group were specially revealing. They found that fouling is caused by H^+ ions generated by even minimal polarization at the surface of anion-exchange membranes. At conditions of polarization, some of the H^+ and OH^- ions from ionization of water are present at the membrane surfaces. As polarization increases, the concentration of H^+ and OH^- ions relative to the total concentrations of ions increases. At the depleting side of anion-exchange membranes, the OH^- ions disappear into the membranes. This leaves H^+ ions remaining in the solution. Any large organic anions in the vicinity of the H^+ ions become associated with the H^+ ions to form the acid of the organic anions. These acids of large organic anions are usually relatively insoluble, and negatively charged precipitates form on the positively charged anion-exchange membranes. When this occurs, a bipolar membrane "sandwich" is formed that gives rise to even faster production of H^+ ions. Thus, once the process of organic fouling is started, it proceeds more and more rapidly with the passage of time.

Korngold and his co-workers also found that the obvious expedient of washing the membranes with alkali solutions while they are in place to reverse the process of formation removed the organic precipitates and restored the original resistances and coulomb efficiencies of the stacks. Cleaning stacks with alkali washes has also been found to be an effective procedure by Olie[13] and by Ahlgren[19] for restoring the performance characteristics of electrodialysis stacks used for treating certain industrial solutions. In the author's laboratory, periodic rinsing with solutions of enzymes has been found to remove some types of colloidal material.

Other findings by the Korngold group were:

—Conditions that minimize excessive polarization (e.g., high solution velocities, spacers with good mixing action) also minimize organic fouling.

—All of the eleven types of membranes they studied were fouled by organic anions, but some membranes were less susceptible to fouling than others. They also found fairly wide variations in susceptibility to fouling between different batches of the same type of membranes.

—Membranes with glossy surfaces were less prone to foul than ones with dull or roughened surfaces.

—Membranes with macro-inhomogeneities were more prone to foul than homogenous membranes.

—Operation of membrane cells under hydrodynamic conditions that minimized polarization also minimized fouling.

Grossman and Sonin[19] not only studied fouling of anion-exchange membranes by organic matter, but also studied the fouling and poisoning of cation-exchange membranes by hydrous ferric oxide. Their findings on organic fouling generally confirmed the findings of Korngold. They also found, as did De Korosy[20] previously, that multivalent cations "poison" cation-exchange membranes by entering the polymeric matrix and associating with the fixed negative charges. In addition, they found that thin films of hydrous oxides deposited on the cation-exchange membranes and formed bipolar membranes. These films could be removed by rinsing with EDTA solutions.

E. Minimizing Polarization

It was stated previously that operating conditions that minimized polarization minimized organic fouling. Minimal polarization is also desirable to prevent or minimize scaling of membranes. Minimal polarization is achieved at high values of the polarization parameter, i/N, which varies with solution velocity and with the nature and shape of the mesh-like spacer materials used to maintain desired spacings between membranes.

Figure 7 shows the change in the polarization parameter, i/N, with nominal solution velocity for several commercial types of spacers, and for an experimental thin-cell spacer just now being commercialized. The data shown are from experiments in which the thickness of the spacer was carefully matched to the cell thickness. (Other data are available in the literature, but because of a lack of correspondence of thicknesses, some of the literature data are questionable.)

The Vexar spacer is indicated to give the best mixing action (i.e., the highest values of i/N) of the eight spacer materials for which data are presented.

It is believed that the good mixing action results from a semi-helical flow path of solution in which first the surface of one membrane and then the surface of the opposite membrane is swept by rapidly moving solution as indicated in Figure 8.

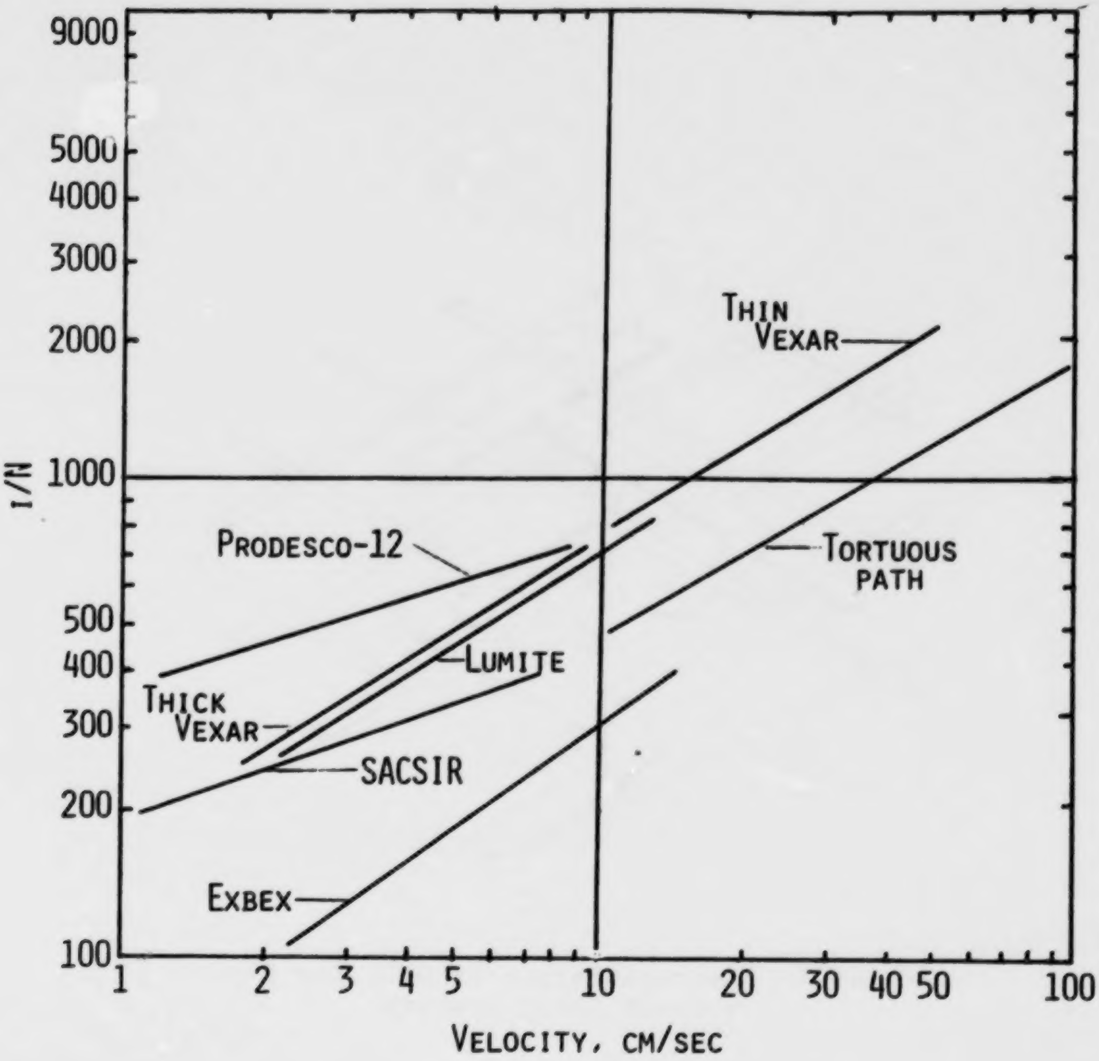


Figure 7. Variation of Polarization Parameters with Velocity for Different Spacers

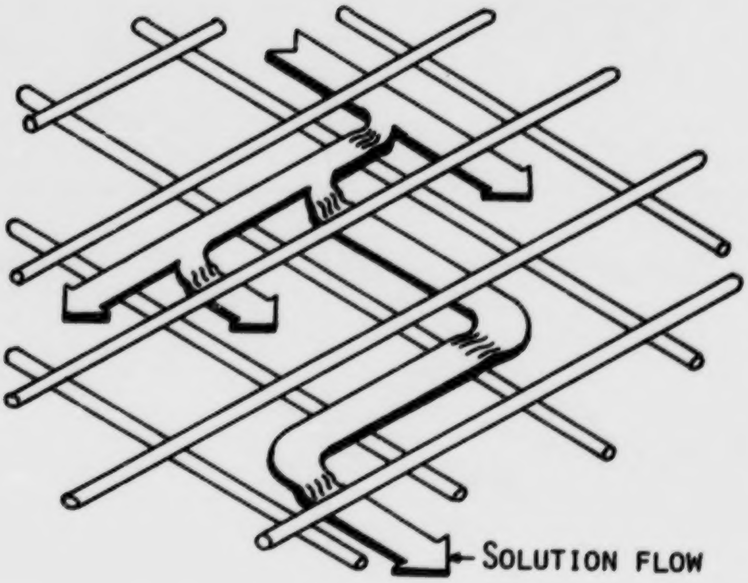

SOLUTION FLOW

Figure 8. Representation of Solution Flow through Vexar Spacers

F. Process Arrangements of Electrodialysis Stacks

Electrodialysis stacks may be used in various ways to achieve different design goals. Mintz[21] has described the process variations in detail. Therefore, they will be discussed only briefly here. Continuous-flow arrangements of stacks are often used for large-scale operations in which the desired degree of demineralization cannot be achieved in one stage. In the continuous-flow arrangement solutions flow through first-stage stacks and directly into second-stage stacks, and from there to third and fourt stages, if needed. This arrangement generally results in low capital cost per unit of productivity, but the arrangement is not very flexible in accomodating changes in feed concentrations, temperatures, or pH.

The batch-recirculation process is more flexible than the continuous-flow process, but the capital cost per unit of productivity is usually higher. In the batch-recirculation process only one stage of stacks is used, and the solutions are pumped from reservoirs through the stage of stacks and back to the reservoirs. The concentration of the depleting stream is decreased during a batch run; that of the concentrating stream is increased.

When large changes in feed-solution concentrations are encountered and a continuous flow of product is required, a feed-and-bleed process is sometimes used. In this process only one stage of stacks is used, and solutions are pumped at high velocity through the stage. A desired portion of the total flow is "bled" from the effluent stream and the remainder is pumped back to the entrance to the stack. At this point an amount of fresh feed equal to that bled from the recirculating stream is introduced. With the feed-and-bleed process feed streams of changing concentration can be treated easily, but the energy requirements are high and sensitive instrumentation is required.

Mintz[21] has presented process descriptions and calculations relating to these and other design variations.

G. Operational Limitations of Electrodialysis Processes

Excessive concentration polarization at the surfaces of the membranes can limit the current densities that can be used in electromembrane processing.

The degree of concentration that can be achieved is limited by the amount of water that is transferred through the membranes along with the ions by osmosis and electroosmosis. The flux of water that occurs with a flux of ions is highly dependent on the nature of the membranes. The concomitant fluxes of water and ions have not been studied extensively, but Lakshminarayanaiah and Lacey[22] here reported some data on the subject. In general the number of milliliters of water transported per faraday decreases with increases in current density, decreases with increases in solution concentration, and decreases as the water content of the membrane decreases.

Another limitation on the degree of concentration that can be accomplished in some applications of electromembrane processing is that some compounds present in the feed solutions may exceed their maximum solubility if the feed is concentrated too much. For example, in the electrodialytic concentration of seawater to furnish brines for the chlor-alkali industry, the formation of precipitates of calcium sulfate in the concentrating compartments limited the degree of concentration that could be achieved. The developers of this process solved the problem by developing ion-exchange membranes that allowed the transfer of Na^+ and Cl^- ions in preference to Ca^{+2} and SO_4^{-2} ions.

In addition to the technical limitations above there is an economic limitation on the degree of depletion that is feasible in some applications of electromembrane processes. As the concentration of electrolyte in the depleting stream decreases, the electrical resistance of the solution increases, I^2R losses increase, and, at some point, an excessive amount of energy becomes necessary to effect additional depletion of the solution and the high costs for energy cause the process to become non-competitive with other types of processing.

H. Applications of Electrodialysis

Electrodialysis processes are used:

- In the food industry-desalting of whey, and sweetening of citrus juices.

- In the chemical industry-concentration of sea water to recover sodium chloride, and recovery of nickel from plating baths.

- In the pharmaceutical industry-desalting of an iron complex.

- In the treatment of wastes-separation of pulping liquor components for reuse, recovery of pickling acids from spent pickle liquor, and recovery of nickel from plating wastes.

II. REVERSE OSMOSIS

Normally, when a membrane that is selective for a solvent separates a concentrated solution from a dilute one, osmosis occurs and solvent molecules transfer from the dilute solution to the concentrated solution. However, if a hydraulic pressure in excess of the osmotic pressure is applied to the concentrated solution, as in Figure 9, the direction of solvent transfer is reversed, and solvent transfers from the concentrated to the dilute solution. The process of reverse osmosis is based on the phenomenon of reversed transfer that occurs when a pressure excess of the osmotic pressure is applied.

In reverse osmosis, each component of the high-pressure solution dissolves in the membrane in accordance with an equilibrium distribution law, and diffuses through the membrane in response to pressure and concentration gradients. An equation has been developed[29] that describes the flux of solvent:

$$J_1 = \frac{D_1 c_1 v_1 (\Delta P - \Delta \pi)}{RT\Delta x}$$

where:
J_1 = flux of solvent
D_1 = diffusivity of the solvent
c_1 = concentration of solvent in the membrane
v_1 = partial molar volume of solvent
R = gas constant
T = temperature
ΔP = difference in applied pressure
$\Delta \pi$ = difference in osmotic pressure
x = thickness of membrane

Note that the net driving force for solvent transfer is the difference between the applied pressure difference and the osmotic pressure difference.

The flux of solute is almost unaffected by the applied pressure and can be described as follows:

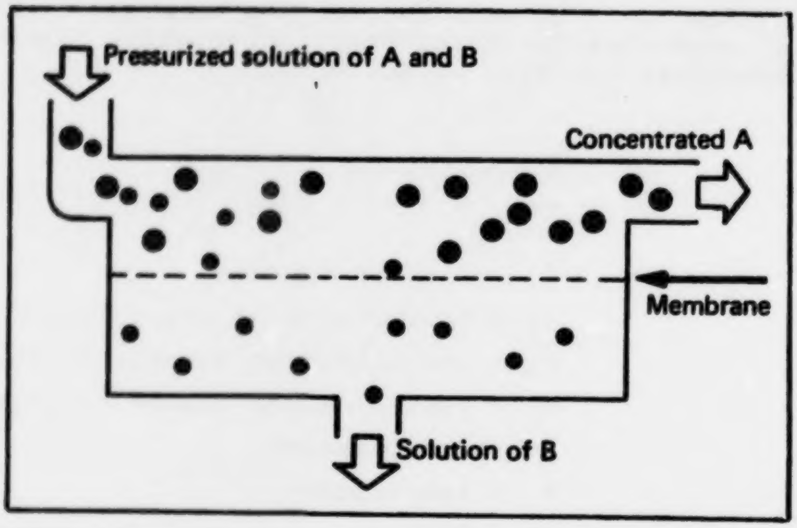

Pressurized solution of A and B
Concentrated A
Membrane
Solution of B

Figure 9. Schematic diagram of Reverse Osmosis Process

$$J_2 = -D_2 \frac{\Delta c_2'}{\Delta x} = -D_2 K \frac{\Delta c_2'}{\Delta x}$$

where: J_2 = flux of solute

D_2 = diffusivity of solute

Δc_2 = concentration difference within the membrane

$\Delta c_2'$ = difference between concentrations in the two solutions

Δx = thickness of membranes

ΔK = distribution coefficient for solute between the membrane and external phases

A. Membranes

The membranes used in the reverse osmosis process are selective for water or other substances capable of hydrogen bonding to the membrane matrix. Water dissolves in the membrane matrix by a hydrogen-bonding mechanism. The polymer from which the membrane is made must be capable of hydrogen bonding to water and still have enough of an organic nature to exclude ions. In addition the polymer must ben an excellent film former, since with the high transmembrane pressure used any pinholes or other imperfections in the films would allow passage of the concentrated solution. Polymers of cellulose acetate, and other cellulose esters are most often used as materials for reverse osmosis membranes. In Figure 10, an attempt has been made to depict the way in which water hydrogen bonds to carbonyl oxygen atoms on cellulose acetate, and transfers from one hydrogen-bonding site to another.

Because of the "tight" structure of the membrane matrix and because of the retarding action of the hydrogen-bonding sites, the resistance to water transfer is high. To achieve reasonably high transfer rates at reasonably low pressures, two-layer membranes have been developed. The two-layer membranes have an extremely thin skin of dense material and a porous underlayer as shown in the scanning electron micrograph in Figure 11. The dense "skin" shown at the top of Figure 11 is the actual selective membrane, and it usually is very thin (0.2 microns). The underlayer, a part of which is shown at the bottom of Figure 11, has relatively large interconnecting pores (0.1 to 0.3 microns diameter) that offer little resistance to the flow of solution once it has transferred through the thin skin. The porous underlayer is usually about 100 microns thick.

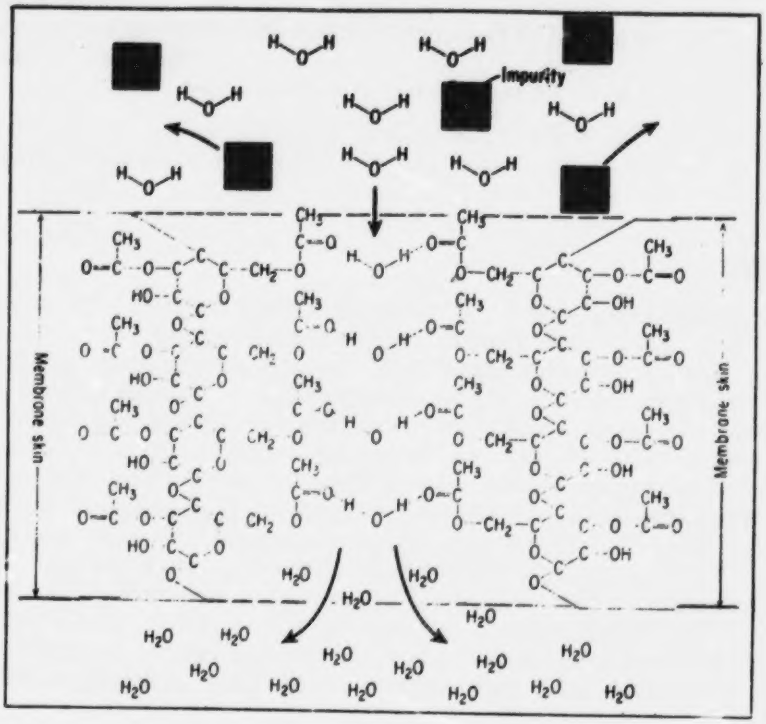

Impurity
H_2O
Membrane skin
Membrane skin

Figure 10. Representation of the ordered structure of Reverse Osmosis Membrane

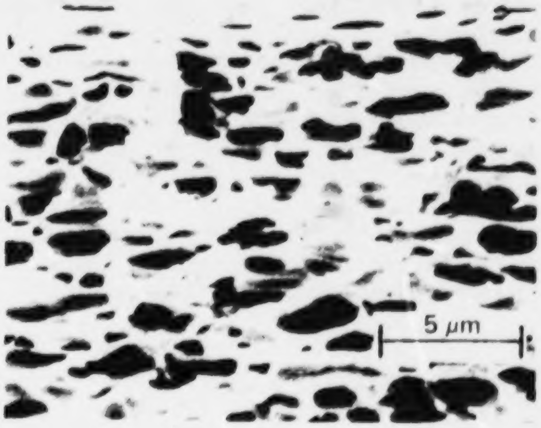


Figure 11. Electron micrograph of Reverse Osmosis Membrane

The two-layer membranes used in many types of equipment are often called Loeb-Sourirajan membranes after the co-discoverers of a practical method of casting and heat-treating the membranes. In this type of membrane the thin skin changes rather abruptly into the porous underlayer as shown in Figure 11. Also used in some types of equipment are hollow-fiber membranes, in which the entire thickness of the membrane (i.e. wall thickness of the hollow fibers) is of the dense material. In addition, membranes made of a thin layer of dense material placed on a separate porous underlayer, and anisotropic hollow-fiber membranes are in an advanced stage of development.

Membranes made of cellulose esters which has been the most used material, has certain limitations discussed below.

Cellulose esters hydrolyze rapidly at either high or low values of pH. Therefore, to achieve long lifetimes of cellulose acetate membranes the solution being treated must be maintained within a fairly narrow range of pH (about 3 to 7.5). Another difficulty encountered with cellulose acetate membranes is that the porous underlayers compact slowly at the operating pressures used and cause the thickness of the thin skin of Loeb-Sourirajan membranes to increase and the size of the pores in the spongy underlayer to decrease. With compaction there is a concommitant decrease in flux. The slow decrease in flux results in increased processing costs, since less product is produced per unit area of membrane.

At temperatures higher than about 50°C (122°F) the polymeric matrix of Loeb-Sourirajan cellulose acetate membranes becomes increasingly ordered. Indeed, the polymeric matrix of the skins on membranes immediately after casting at low temperatures have a low degree of ordering, and have low salt rejections. The salt rejections are improved by holding the membranes at specified high temperatures (in the range of 60° to 80° C) for predetermined periods. This "annealing" process causes the skins to become less amorphous and more ordered. However, because of the tightening of the thin skin at temperatures above 50°C (122°F), the highest operating temperature useable with cellulose acetate membranes is about 120°F.

Because of the above limitations of cellulose acetate membranes, much study has been given to the development of other polymeric materials for making reverse osmosis membranes that do not have these limitations. Space permits a mention of only some of the more promising materials: the aromatic polyamides that are used for one type of hollow-fiber membrane; polybenzimidazoles,[24] poly(phenylene oxide),[25] crosslinked polyvinylpyrrolidone,[26] and polyethylenimine-coated membranes.[27] The last-named appears to be stable over a pH range of 1 to 13.

B. Concentration Polarization

Concentration plarization occurs in reverse osmosis, as in any process with selective membranes. As water transfers through the water-selective membrane solutes are left behind. The solutes increase the concentration of the solution at the solution-membrane interface on the high-pressure side of the membrane. A concentration gradient is established in the boundary layer that acts as a driving force for diffusion. The concentration increases until at steady state the transfer of solutes to the bulk of solution by diffusion just equals the amount of solutes left behind by the selective transfer of water. The back osmotic pressure, which diminishes the driving force due to the applied pressure, is proportional to the difference between the solute concentrations at the interfaces of the membrane. Therefore, any increase in concentration at the interface on the high-pressure side diminishes the driving force for transfer of water, and is undesirable.

To minimize concentration polarization at membrane interfaces, high solution velocities and various types of turbulence promoters are used to decrease the thicknesses of diffusive boundary layers. Many of the studies of boundary-layer control in reverse osmosis have been recently reviewed.[27] Therefore, no detailed discussion is presented here.

C. Types of Membrane Permeators

The four main types of membrane permeators are, plate-and-frame, tubular, hollow fiber, and spiral-wound types.

1. Plate-and-Frame Units

In the plate-and-frame type of construction thin plastic plates with spiral grooves or mesh spacers are covered on both sides with selective membranes and the membranes are cemented at the edges to prevent leaks, as indicated in Figure 12. These membrane-covered plates are then stacked atop each other like a stack of dishes, and encased in a vessel that can withstand the pressure to be applied. Each membrane covered plate is provided with a mechanism (usually spiral grooves) to lead the permeate to a central collecting pipe, which may also serve as a means of indexing the plates. A number of variants of the plate-and-frame system have been developed.

In comparison with other designs the plate-and frame design has good volumetric efficiency and high fluxes. However, skilled assemblers are needed when membranes must be replaced, the capital cost per unit of productivity is relatively high, and the probability of leaks and other defects is high.

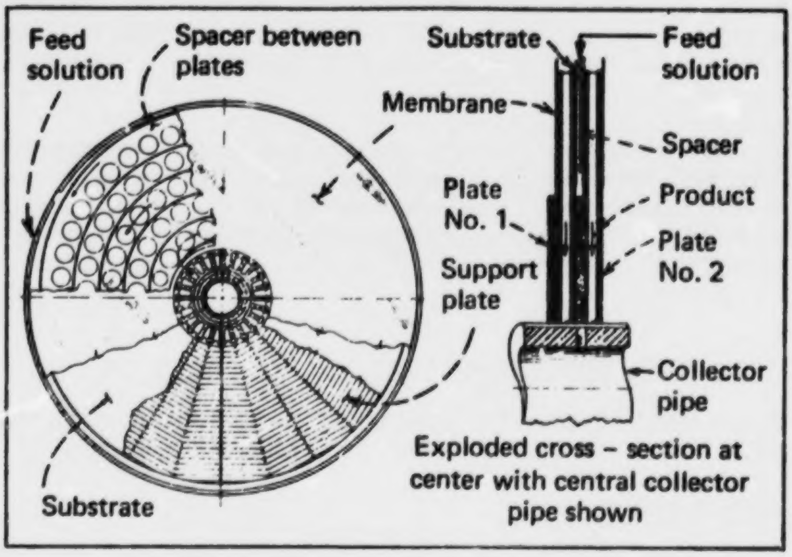

Feed solution
Spacer between plates
Membrane
Substrate
Support plate
Substrate
Feed solution
Spacer
Product
Plate No. 1
Plate No. 2
Collector pipe
Exploded cross - section at center with central collector pipe shown

Figure 12. Plate-and-frame Membrane Permeator

2. Tubular Units

Although tubular units can be made with the membranes on the outside of porous support tubes, most tubular units have the membranes inside the tubes. Therefore, this discussion will be confined to tubular units with membranes inside the tubes. In these units porous tubes that are strong enough to withstand the operating pressures are used, since the tubes both contain the pressure and permit transfer of water that permeates the membrane. Tubes have been made of glass fibers bonded with thermosetting resins, granular materials bonded with thermosetting resins, and perforated metal.

Membranes are either cast directly on porous supports inside the tubes, or cast separately and inserted into the tubes. The solution to be treated is pressurized and pumped through the tubes. Permeate transfers through the membranes, through the porous support (if one is used) and then through the tube wall, as indicated in Figure 13. The permeate from a number of separate tubes is usually collected, and removed. Individual tubes, which might be only 10 to 20 ft long, may be interconnected in series, parallel, or combinations of series-parallel arrangements.

The main advantages of tubular units are: they can handle feed solutions with high contents of particulate matter, they can be very easily cleaned, and they are only moderately expensive per unit of productivity. On the other hand, membrane replacement is relatively expensive, since many fittings and connections must be dealt with in dismantling and reassembly, and there is some risk of leaks at the many interconnections.

There are a number of designs of tubular units that differ in the types of porous supports and turbulence promoters used.

3. Hollow-fiber Units

The basic element of these units is a fine hollow fiber (25 to 40 microns I.D. and 50 to 80 microns O.D.) of the selective membrane material itself. Fibers as fine as this can withstand high pressures without collapsing. A mass of these fibers are aligned into a U-shape and the open end of the "U" is encapsulated in a resin. Grooves are formed in the encapsulating resin to receive a retaining ring that fits tightly in a cylindrical pressure vessel, when the end of the U-shaped mass of fibers is placed into the cylinder as indicated in Figure 14. The final result is a membrane permeator that resembles a U-bend shell-and-tube heat exchanger except that the "tubes" are extremely fine fibers. Feed solution is introduced through a perforated tube that extends axially near the center of the mass of fibers. Some of the solution permeates the fibers and is withdrawn from the

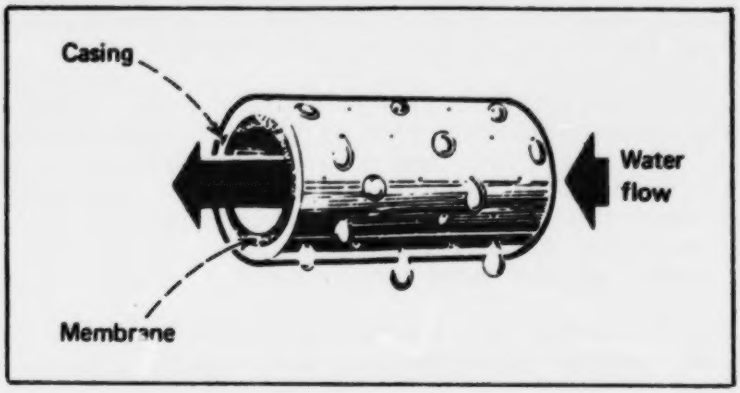

Casing
Water flow
Membrane

Figure 13. Diagram of a Tubular Membrane Permeator

end of the cylindrical pressure vessel opposite to the feed-introduction end. The concentrated brine left behind on the outside of the fibers flows through the shell into a collector pipe at the feed-end of the vessel.

The main advantages of the hollow-tube units is low cost and small space requirements per unit of productivity. Because the hollow fibers are self-supporting and can be produced cheaply, a vast area of membrane can be encompassed in a small volume and can be put into production at low cost. Thus, even though the permeation rates per unit of area are low relative to that through anisotropic membranes (perhaps 1/50th the rate), the permeation rate per dollar invested might be the same, or higher. On the other hand the mass of hollow fibers is fairly efficient as an in-depth filter and feed solutions often must be pre-treated to remove particulate material.

4. Spiral-wound Units

In spiral-wound modules a 4-layer sandwich comprised of a spacer material, a membrane, a porous material to collect permeate, and another membrane is wound spirally around a perforated center pipe that acts as a permeate collector, as indicated in Figure 15. One or more spiral modules are mounted in a cylindrical pressure vessel and a number of the cylindrical pressure vessels may be interconnected in series, parallel, or combination of series-parallel, as shown in Figure 16. Feedwater flows axially through the spaces made by the spirally-wound mesh spacer. Some of the solution permeates the membranes and enters the porous permeate space. The permeate travels spirally inward, enters perforated holes in the central collector pipe, and is withdrawn through this pipe.

The capital cost of spiral-wound units per unit of productivity is relatively low, and the volumetric and space requirements are low. Instead of replacing membranes, pre-assembled modules are replaced. With these units, as with the hollow-fiber units particulate matter in the feed solutions can pose a problem, and pretreatment to remove particulate matter may be necessary.

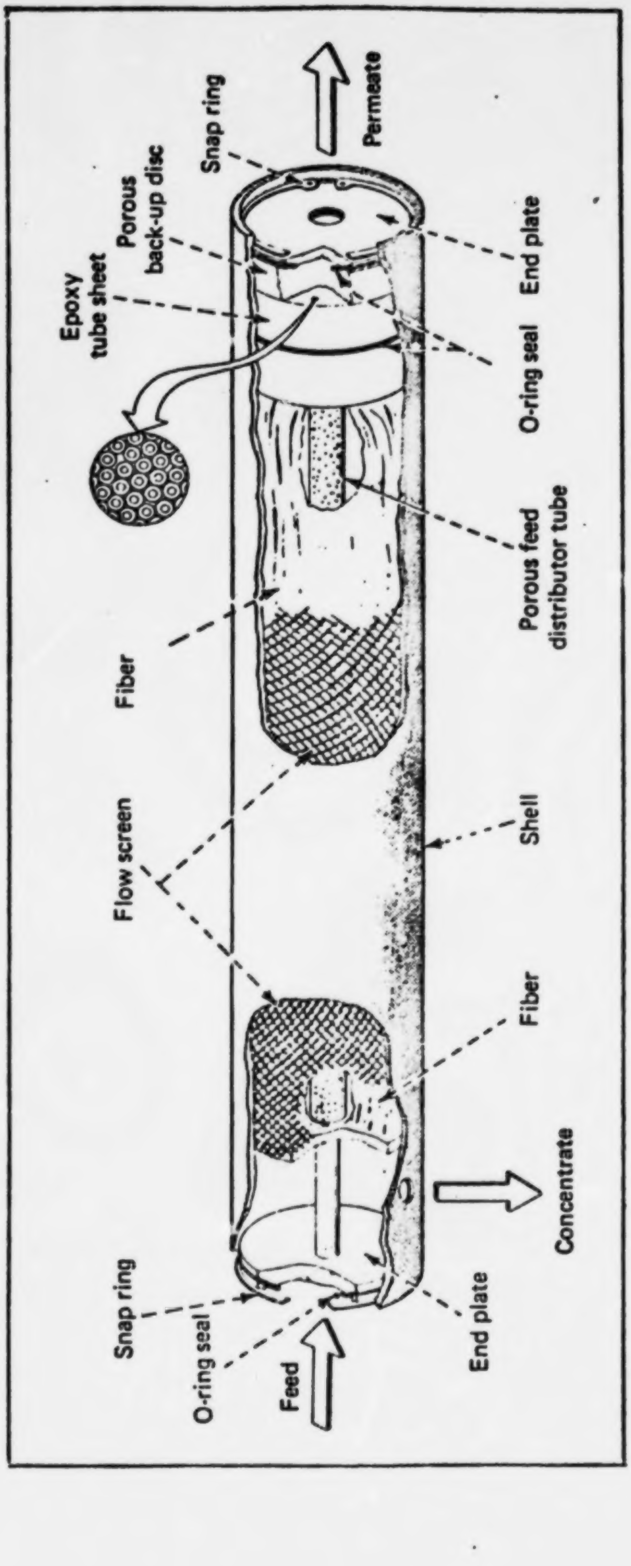
D. Applications for Reverse Osmosis

Reverse osmosis is suited for treating wastewaters containing heavy metals, and other papers in this symposium will deal with that subject in detail. Among the other applications that might be listed for reverse osmosis are:

- In the food industries - concentration of fruit juices, coffee, tea, milk and syrups.

- In the chemical industry-fractionation of azeotropes, and molecular weight fractionation.
- In the pharmaceutical industry - concentration of antibiotic beers, and concentration of enzyme solutions.
- In medicine - preparation of high-purity water for use in artificial kidneys.
- In the treatment of wastes - treatment of dilute solutions in the pulp industry, treatment of drag-out rinses in the metal-plating industry, and the recovery of protein and lactose from whey in the cheese industry.

Obviously, the above list includes only a few of the potential uses for reverse osmosis, and other uses will be apparent.


Feed
O-ring seal
Snap ring
End plate
Concentrate
Fiber
Flow screen
Shell
Fiber
Porous feed distributor tube
Epoxy tube sheet
Porous back-up disc
O-ring seal
End plate
Snap ring
Permeate

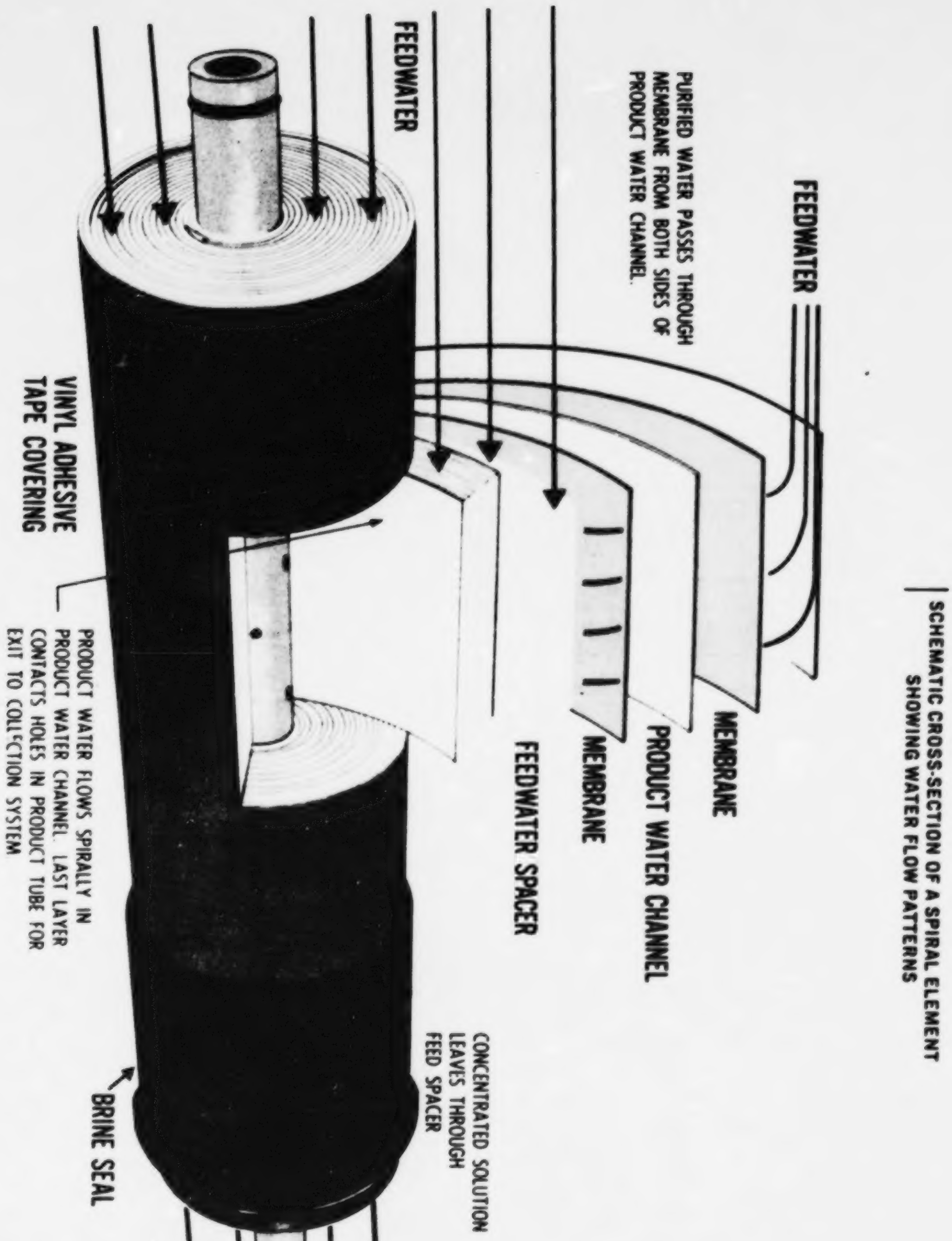

SCHEMATIC CROSS-SECTION OF A SPIRAL ELEMENT SHOWING WATER FLOW PATTERNS
FEEDWATER
MEMBRANE
PRODUCT WATER CHANNEL
MEMBRANE
FEEDWATER SPACER
PURIFIED WATER PASSES THROUGH MEMBRANE FROM BOTH SIDES OF PRODUCT WATER CHANNEL.
FEEDWATER
VINYL ADHESIVE TAPE COVERING
PRODUCT WATER FLOWS SPIRALLY IN PRODUCT WATER CHANNEL. LAST LAYER CONTACTS HOLES IN PRODUCT TUBE FOR EXIT TO COLLECTION SYSTEM
CONCENTRATED SOLUTION LEAVES THROUGH FEED SPACER
BRINE SEAL
CONCENTRATE
PRODUCT

Figure 15. Diagram of a Spiral-wound Membrane Permeator

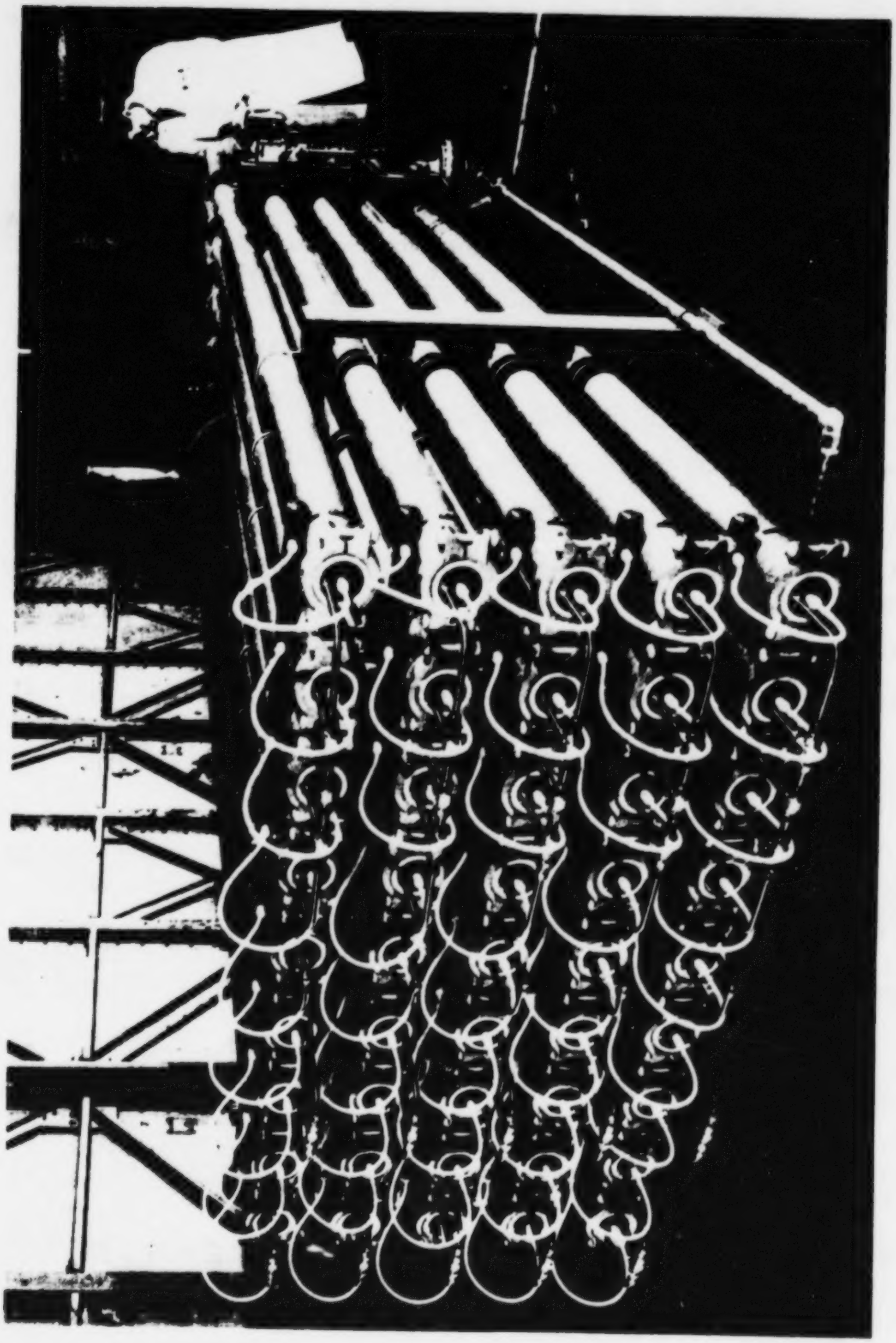


Figure 16. A 100,000 gpd Spiral-wound Modular Unit

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REMOVAL OF TRACE HEAVY METAL IONS FROM WATER BY ELECTRODIALYSIS

by

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Presented at the Conference "Traces of Heavy Metals in Water:
Removal Processes and Monitoring", Princeton University,
November 15, 1973

INTRODUCTION

Electrodialysis is a process for separating low molecular weight electrolytes from solutions or suspensions containing essentially unionized substances for example, water. The low molecular weight electrolytes, which must be at least partially ionized, are caused to pass through ion exchange membranes having a relatively low hydraulic permeability. This process will remove traces of heavy metals ions (as well as otherions) from water to any degree desired and generally concentrate them in solution in a rinse stream to levels at which they can be readily handled by conventional methods, e.g., precipitation and ultimate disposal as the sulfides, hydroxides, carbonates, sulfates or phosphates. In this paper such trace heavy metals are assumed to be chromium, manganese, cobalt, copper, zinc, arsenic, cadmium, antimony, barium, mercury, thallium and lead

We will first discuss the nature of ion exchange membranes and the properties which are important to electrodialysis. This will be followed by a general description of the process and apparatus and a discussion of the relevant economics.

ION EXCHANGE MEMBRANES (Exhibit 1)

Ion exchange membranes are ion exchange resins in sheet form. Typically they are based on crosslinked polystyrene and are therefore chemically stable and insoluble in the usual solvents. Typical commercial membranes are about 0.022 inches thick, 18 inches wide and 40 inches long and are reinforced with inert woven fabrics to provide desirable physical properties.

There are two types of membranes. Cation exchange membranes contain negatively charged groups such as sulfonate groups chemically bonded to the polystyrene. The membranes are electrically neutral and contain positively charged counterions such as sodium, calcium, hydrogen or trace heavy metal cations equivalent to the number of fixed negatively charged groups. When the membranes are equilibrated with water or aqueous solutions they will absorb from 20 to 70 percent by weight of water. The water content is fixed during manufacture and is reasonably independent of external solution concentrations. This so-called gel water is more or less homogeneously distributed throughout the membrane in pores which have average diameters in the range of about 1 to 10 nanometers. The average pore diameter is fixed during manufacture. These pores are thus in the range of typical diameters of soluble molecules. Membranes having pores on the low end of the range, e.g. 1 to 2 nanometers, are most advantageously used in electrodialysis.

The second classification of membranes, anion exchange membranes, contain positively charged groups such as quaternary ammonium groups chemically bonded to the polystyrene. These membranes also contain mobile negatively charged counter-ions such as chloride, sulfate, bicarbonate or trace heavy metal anions. The description of the solvent in cation exchange membranes is entirely applicable to anion exchange membranes.

The counterions, that is, cations in cation exchange membranes or anions in the anion exchange membranes, are substantially dissociated from the fixed charged groups and are free to migrate throughout the membrane as long as electroneutrality is maintained. These mobile ions give rise to the ion exchange properties of the membranes since they may be exchanged for other mobile counterions including trace metal ions by contacting the membranes with solutions of salts of such ions.

In the presence of an electrical potential gradient, electric current is carried by the mobile counterions. The sulfonate (or quaternary ammonium ions) which are chemically bonded to the polymer structure may be regarded as subject to the same electrical potential gradient but are not free to move in the gel water of the membrane and therefore do not participate in carrying the electric current. Hence the current is carried substantially completely by counterions. Commercial membranes are good conductors; the specific electrical resistances generally are a few hundred ohm cms and the areal resistances are about 10 ohm cm^2 or 0.01 ohm $foot^2$.

Considerable frictional interaction takes place between the counterions and gel water. Under the influence of a potential gradient, the gel water migrates in the same direction as the counterions. This phenomenon is known as electroosmosis. Substantially all of the gel water in a membrane participates in electroosmosis, the rate of migration depending upon the magnitude of the potential gradient, the average pore size of the membranes and the nature of the counterion. The specific electroosmotic property of a membrane is expressed as the number of milliliters of water accompanying the passage of 26.8 ampere hours (one electrochemical equivalent). This quantity may be varied during manufacture from about 50 milliliters to about 750 milliliters of water per electrical equivalent.

ELECTRODIALYSIS APPARATUS FOR DEMINERALIZATION (Exhibit 2)

The basic apparatus for electrodialysis consists of a stack of membranes between two electrodes. Flow of the process streams is contained and directed by spacers which alternate with the membranes. The spacers are generally about 40 mils thick. The stack is internally manifolded by lining up apertures in the membranes and spacers. The assembly of membranes, spacers, and electrodes is held in compression by a pair of end plates located outboard of the electrodes and connected by tie rods. The assembly thus resembles a plate and frame filter press containing about 16 membranes per linear inch. The stack is typically 38 by 18 by 40 inches and contains 3000 square feet of membrane which is roughly 200 square feet of membrane per cubic foot.

For demineralization (including removal of trace heavy metal ions) the membranes in the stack are arranged alternately cation and anion. The unit composed of a cation membrane, a spacer, an anion membrane and another spacer is a repeating unit termed a "cell pair". An electrodialysis stack may contain 300 or more cell pairs between a single pair of electrodes. This stack is diagrammed in Exhibit 2.

A direct current potential of about one volt for each membrane is applied to the stack of membranes and spacers. The current which flows then depends on the electrical conductivity of the solution between the membranes and is typically in the range of 20 to 150 amperes per square foot. The current passes in series through all the membranes and solution compartments and is therefore "used" many times before passing out of the electrodialysis stack.

The compartments which have an anion membrane on the anode side and a cation membrane on the cathode side are demineralizing, compartment (heavy metal decontaminating compartments) while the alternate compartments are concentrating or rinse compartments. There are thus two kinds of compartments also arranged in alternation. A solution which we wish partially to demineralize, for example, to remove trace heavy metal ions, is passed continuously through the demineralizing compartments and a rinse stream is passed continuously through the concentrating compartments. Upon the application of the direct current, low molecular weight electrolyte (including trace heavy metal ions and some water) will pass from the demineralizing compartments into the concentrating compartments. The rinse stream may be recycled to build up the concentration of heavy metal ions to a level convenient for further processing.

Since the transference number of the ions passing through the membrane is nearly unity in the membrane but approximately 0.5 in the solution, about half of the ions must be transferred from the bulk solution in the demineralizing compartment to the membrane surface by diffusion and convection. At low current densities and high bulk concentrations, diffusion is adequate while at high current densities and low bulk concentrations the only adequate process is forced convection. This forced convection is produced by turbulence promoting obstructions in the flow channels of the spacers. It may be further enhanced by increasing the velocity of flow across the membrane surface.

As pointed out above the magnitude of the current will depend upon the conductivity of the solutions in the compartments and therefore on the salinity and viscosity of the solution. Owing to the necessity of dissipating heat from the membranes and electrodes, the current is generally not allowed to exceed 150 amperes per square foot though commercial membrane applications do exist in which the current density is about 800 amperes per square foot.

There are three possible modes of operating such an electrodialysis stack. In "Feed-and-Bleed", part of the product is recycled to the feed inlet, the amount of recycle depending upon the degree of demineralization required. This mode is useful if the required degree of demineralization is not too high. In "Batch" operation the product is returned to a feed reservoir which is periodically charged, demineralized to the required degree and then emptied. This is useful where a low product production rate is required. In "Continuous" operation if the degree of demineralization in one stack, for a given current density and velocity, is less than that required, sufficient stacks are arranged in series to meet the requirement. The degree of decontamination of trace heavy metal ions in any application will be approximately the same as the degree of demineralization of all electrolytes in that applications.

ELECTRODIALYTIC DEMINERALIZATION OF WATER (Exhibit 3)

Almost 400 electrodialysis plants have been sold by Ionics.

The principal commercial application of these plants has been the demineralization of brackish water.

Details of some of these plants are given in Exhibit 3. Of particular interest are the plants at Buckeye, Arizona (the first municipality to have its entire water supply demineralized by electrodialysis); at Siesta Key, Florida (the largest operating municipal electrodialysis facility in the U.S.), and at Foss Reservoir, Oklahoma (the largest demineralization plant sold in the United States). Data on operating costs of the Siesta Key plant are presented below.

A recent development has been the use of electrodialysis for production of very pure water for boiler feed and electronic component washing.[2] It is now feasible to produce water containing as little as 2 to 5 ppm total dissolved solids from water containing 500 to 1000 ppm by electrodialysis.

COSTS OF ELECTRODIALYTIC DEMINERALIZATION (Exhibits 4 through 7)

Approximate capital cost per unit capacity is shown in Exhibit 4. There are two major factors influencing costs: plant capacity and number of stages. The cost per unit capacity decreases slowly as plant capacity increases. Cost increases with the number of stages in series. Determination of the number of stages required depends upon the desired degree of demineralization, approximately the same as the desired degree of decontamination of heavy metal ions. A demineralization of about 50% per stage appears most desirable for engineering reasons. The number of stages then depends upon the desired overall degree of demineralization. Exhibit 4 illustrates the relationship between capacity, number of stages and investment cost. If divalent ions (Ca^{++}, Mg^{++}, $SO_4^{=}$) predominate in the feedwater, each stage will yield a smaller degree of demineralization.

Electrical power requirements can be calculated rather precisely given the feedwater composition. Membrane replacement in most locations is less than 20% per year and with favorable operation less than 10%/year. Replacement costs can also be estimated for pretreatment equipment (if any) to remove suspended solids, electrodes and other components.

Estimation of labor cost depends on local factors and it frequently involves non-technological factors. Operating labor is used primarily for monitoring of equipment and pretreatment if required. This generally requires about one-half man-hour per day for plants below 10,000 GPD. In large plants 2 to 4 man-hours per day may be required. Maintenance labor is estimated at 100 man-hours per stack year for the first stage, 75 for the second, and 50 for subsequent stages. The requirement for maintenance labor depends strongly on the cleanliness of the feedwater.

These costs can be added to produce a total product water cost. Exhibit 5 presents an approximation of total water costs per 1000 gallons as a function of plant capacity and number of stages for a 500 ppm feed.

These predictions can be compared to operating costs for the Siesta Key, Florida plant mentioned above. This plant is basically a 2 million GPD plant for which 60% of the stacks were installed in 1969, a further 15% in 1970, and an additional 15% in 1972. The plant reduces a 1400 ppm water to 500 ppm. Operating costs are given in Exhibit 6. The cost estimate is based on a spot check of actual costs against the supplier's guarantees. The former have consistently been found to be lower. The data in the table are the guarantee figures. Total water costs are given in Exhibit 7. Note that power costs are only about 5¢ out of a total of 29¢ per thousand gallons for the 1400 ppm feed in this plant. If the feed water were 500 ppm at the same degree of demineralization power costs would be reduced to about 2¢ and overall costs to about 25¢.

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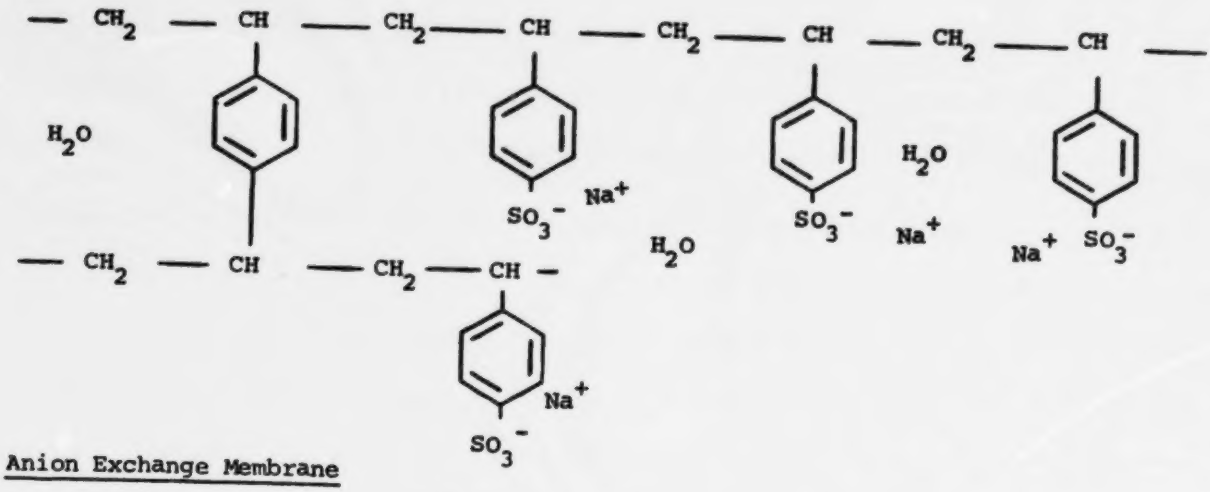
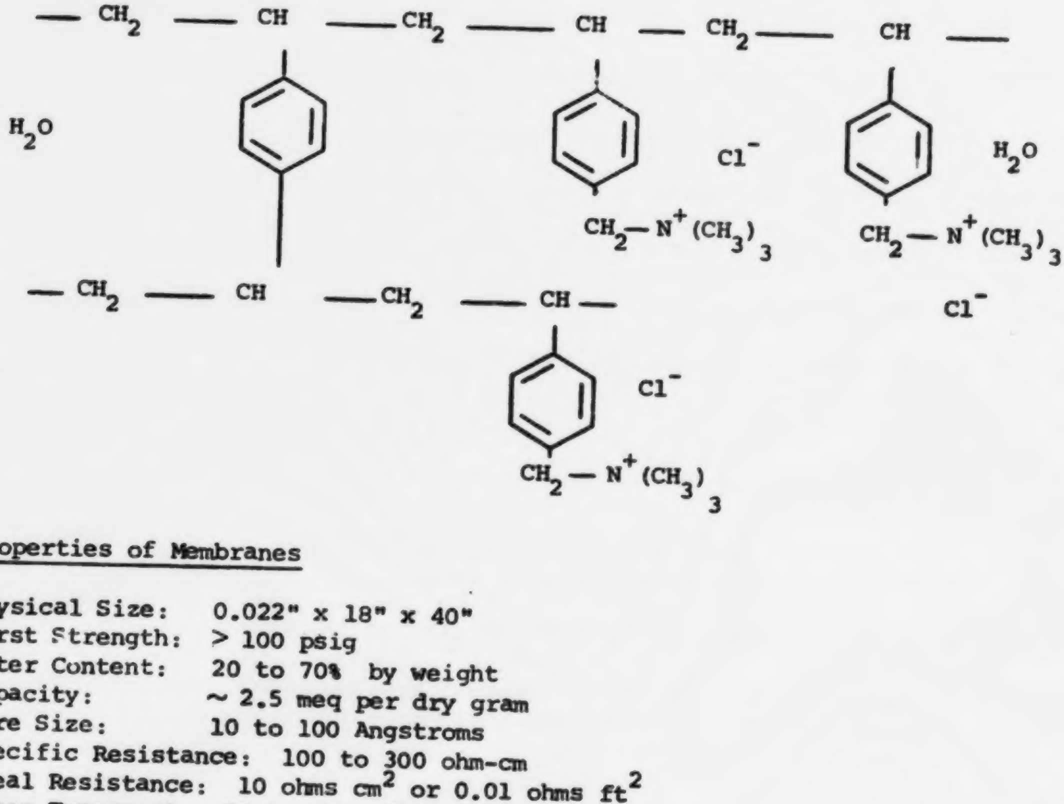
Exhibit 1

STRUCTURE AND PROPERTIES OF ION EXCHANGE MEMBRANES

Cation Exchange Membrane


CH2
CH
H2O
SO3-
Na+
H2O
SO3-
Na+
Na+
SO3-
Na+
SO3-

Anion Exchange Membrane

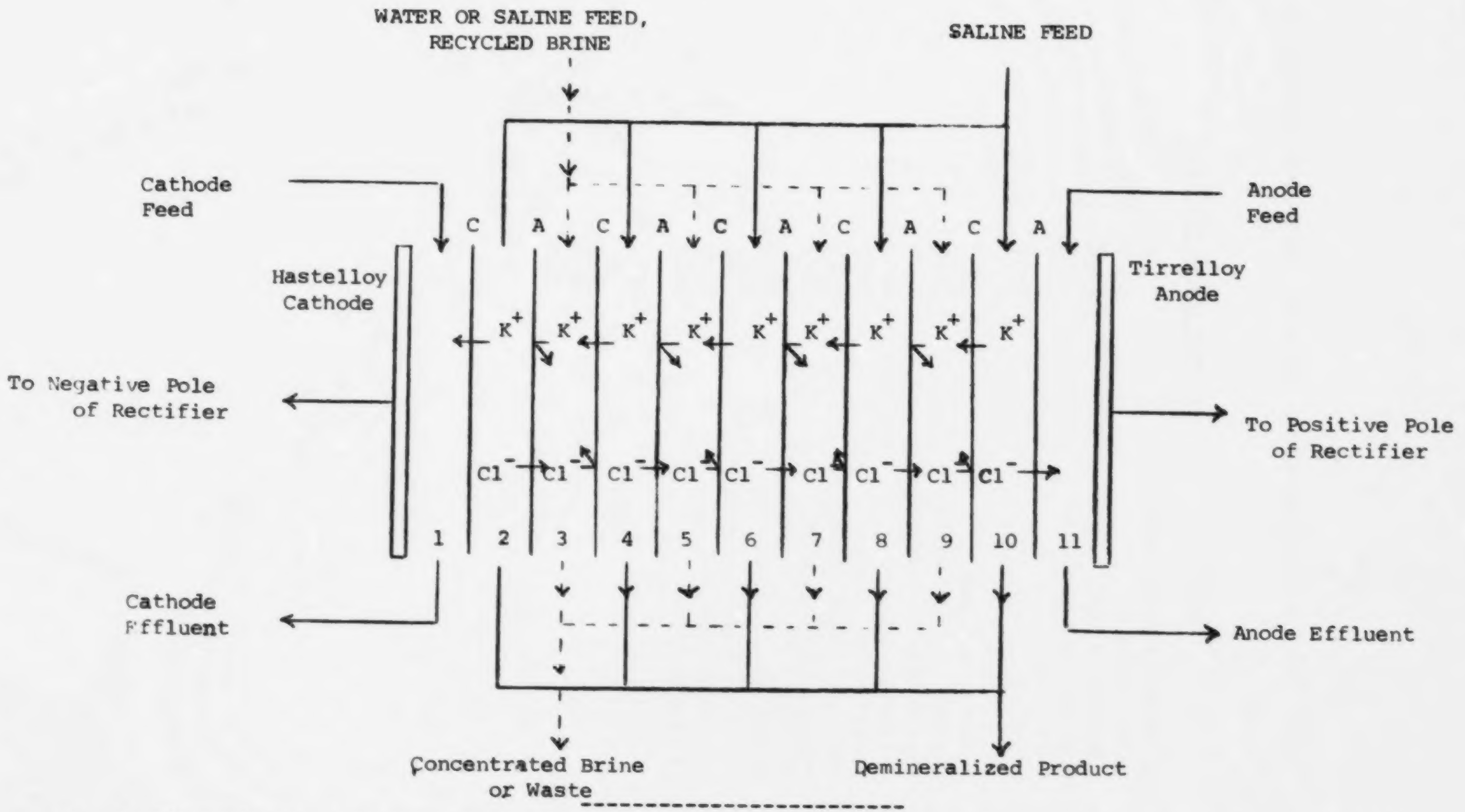

CH2
CH
H2O
Cl-
H2O
CH2— N+ (CH3)3
CH2— N+ (CH3)3
Cl-
Cl-
CH2 — N+ (CH3)3

Properties of Membranes

Physical Size: 0.022" x 18" x 40"
Burst Strength: > 100 psig
Water Content: 20 to 70% by weight
Capacity: ~ 2.5 meq per dry gram
Pore Size: 10 to 100 Angstroms
Specific Resistance: 100 to 300 ohm-cm
Areal Resistance: 10 ohms cm^2 or 0.01 ohms ft^2
Water Transport: 50 to 750 mℓ/Faraday

Exhibit 2

SCHEMATIC DIAGRAM OF ELECTRODIALYTIC DEMINERALIZATION


WATER OR SALINE FEED,
RECYCLED BRINE
SALINE FEED
Cathode Feed
Anode Feed
C
A
C
A
C
A
C
A
C
A
Hastelloy Cathode
Tirrelloy Anode
K+
Cl-
To Negative Pole of Rectifier
To Positive Pole of Rectifier
1
2
3
4
5
6
7
8
9
10
11
Cathode Effluent
Anode Effluent
Concentrated Brine or Waste
Demineralized Product

Up to 600 membranes between one set of electrodes
3.5 sq.ft. active area per membrane
D.C. potential: 1 volt per membrane
Current density: 20 to 150 amps/ft^2

Separated by tortuous path spacers 0.040" thick
Turbulence promoters in spacers
Water transfer: cations - 150 ml per Faraday
anions - 100 ml per Faraday

Exhibit 3

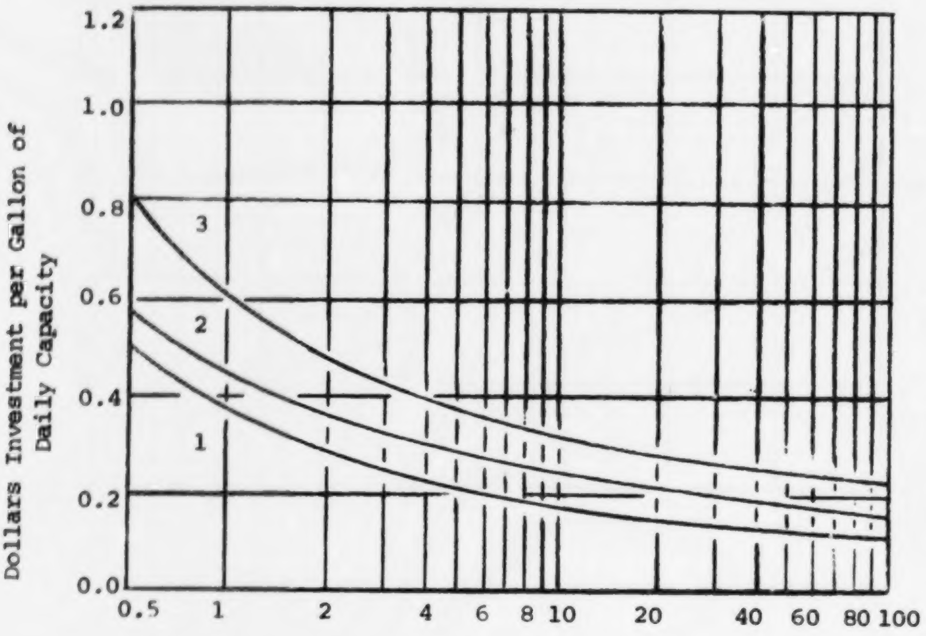
Large Electrodialysis Plants Built or Under Construction by Ionics

Site	Date of Start-Up	M G D
Al Khobar, Saudi Arabia	1967	0.10
Almer, Algeria	1973	1.00
Anaconda Copper, Chile	1970	0.27
Bahrain, Arabian Gulf	1964	0.10
Bari, Italy	1970	0.53
Brindisi, Italy	1971	1.30
Buckeye, Arizona	1962	0.65
Dhahran, Saudi Arabia	1961	0.12
Foss Reservoir, Oklahoma	1974	3.00
Gillette, Wyoming	1972	1.50
Pantelleria, Italy	1973	0.27
Port Mansfield, Texas	1965	0.27
Riyadh, Saudi Arabia	1973	0.64
Sanibel Island, Florida	1973	1.20
Siesta Key, Florida	1969	1.80
State of Kuwait, Persian Gulf	1963	0.24
U.S. Army, New Mexico	1970	0.10
Van Horn, Texas	1969	0.88

Exhibit 4

Approximate Electrodialysis Capital Investment As a Function of Capacity for Various Numbers of Stages

(Each Stage Removes Approximately 50% of Salts in its Feed Water)



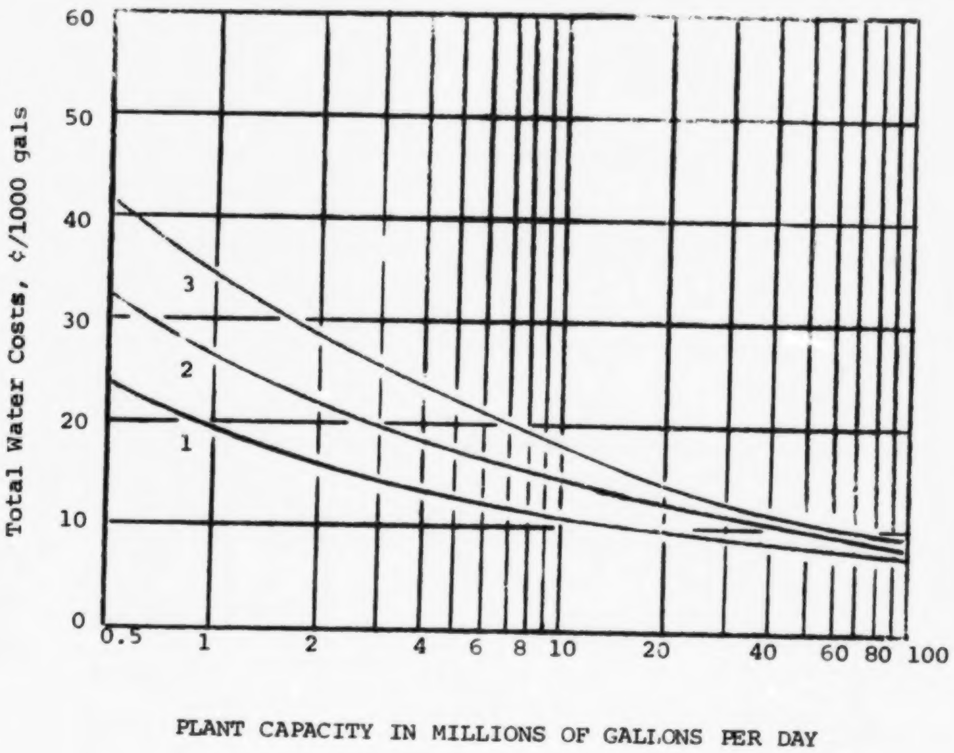
PLANT CAPACITY IN MILLIONS OF GALLONS PER DAY

1 = One Stage, approximately 50% demineralization
2 = Two Stages, approximately 75% demineralization
3 = Three Stages, approximately 87.5% demineralization

Exhibit 5

Total Water Costs, ¢ for 1000 Gallons for 500 ppm Feed
As a Function of Capacity for Various Numbers of Stages

**(Each Stage Removes Approximately 50%
of the Salts in its Feed Water)**



1 = One Stage, approximately 50% demineralization

2 = Two Stages, approximately 75% demineralization

3 = Three Stages, approximately 87.5% demineralization

Exhibit 6

Operating Costs Excluding Labor

	Siesta Key, Florida Ionics Guarantee	
Membrane Replacement	5.8 ¢/Kgal	32.5%
Electrical Power	5.1	28.5
Filters	3.0	17
Other Spare Parts	2.2	12.5
Acid	1.4	8
Miscellaneous	0.3	1.5
Total	17.8 ¢/Kgal	100.0%

Exhibit 7

Total Water Costs

	Siesta Key, Florida Authors' Estimate	
Operating Costs Labor	18 ¢/Kgal	62%
Amortization of Capital	11	38%
Total	29 ¢/Kgal	100%

REVERSE OSMOSIS FOR THE REMOVAL OF HEAVY METALS FROM WASTE WATER:

PRELIMINARY RESULTS

BY

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TRACES OF HEAVY METALS IN WATER:
REMOVAL PROCESSES AND MONITORING
NOVEMBER 15 - 16, 1973

INTRODUCTION

THE CURRENT EMPHASIS ON EFFLUENT GUIDELINES LEADING TO "ZERO DISCHARGE" HAS STIMULATED INTEREST IN ADVANCED WASTEWATER TREATMENT TECHNIQUES.

CURRENT EFFLUENT GUIDELINES FOR THE METAL FINISHING INDUSTRY HAVE BEEN SET FOR COPPER AT 0.2 MG/L, CHROMIUM 6 AT 0.05 MG/L AND NICKEL AND MANGANESE AT 1.0 MG/L.(1)

TO MEET THESE EFFLUENT STANDARDS, WATER MUST BE TREATED TO A HIGH QUALITY WHICH OFTEN MAKES THE REUSE OF WASTEWATER ATTRACTIVE.

REVERSE OSMOSIS HAS RECEIVED WIDE ATTENTION AS A CONCENTRATION PROCESS WHICH IS CAPABLE OF REMOVING A WIDE VARIETY OF DISSOLVED SALTS INCLUDING HEAVY METALS.

MOST FULL SCALE REVERSE OSMOSIS SYSTEMS AT THE PRESENT TIME TREAT POTABLE OR BRACKISH WATER. IN THIS SERVICE THE PERFORMANCE AND ECONOMICS OF THE SYSTEM CAN BE PROJECTED WITH A HIGH DEGREE OF CERTAINTY. IN WASTEWATER APPLICATIONS, HOWEVER, IT IS NECESSARY TO TEST THE PERFORMANCE OF THE SYSTEM TO ADEQUATELY DETERMINE MEMBRANE LIFE AND THE QUALITY OF WATER PRODUCED.

A SUFFICIENT QUANTITY OF PRODUCT WATER SHOULD BE PRODUCED FOR DIRECT EVALUATION IN THE PLANT MANUFACTURING PROCESSES.

GULF DEGREMONT IS CURRENTLY OPERATING A 36,000 GALLON PER DAY REVERSE OSMOSIS PILOT PLANT TO DETERMINE THE FEASIBILITY AND ECONOMICS OF DIRECT RECYCLE OF WASTE WATERS FROM AN ELECTRONICS MANUFACTURING PLANT.

THIS PAPER REPORTS INITIAL RESULTS OF HEAVY METAL REMOVALS FROM THIS WASTEWATER.

PLANT WASTE WATER TREATMENT

THE EXISTING WASTE WATER TREATMENT PLANT IS SHOWN IN FIGURE 1. WASTE WATER, INCLUDING ION EXCHANGE REGENERANTS AND EFFLUENTS FROM THE CHROMIUM AND CYANIDE DESTRUCTION SYSTEMS, IS COLLECTED AND PUMPED TO A HOLDING TANK.

FROM HERE THE WATER IS PUMPED TO A LIME ADDITION SYSTEM AND TO A SOLIDS CONTACT CLARIFIER. LIME IS ADDED TO A pH OF APPROXIMATELY 9 - 10 AND POLYELECTROLYTE IS FED TO THE CENTER WELL.

SLUDGE IS BLOWN DOWN FROM THE CLARIFIER TO VACUUM FILTERS AND THE CAKE IS HAULED TO LAND FILL.

THE CLARIFIED WATER IS THEN pH ADJUSTED TO APPROXIMATELY 6.5 TO 8.0 USING SULFURIC ACID AND IS DISCHARGED.

THE MAJOR PART OF THE HEAVY METALS ARE REMOVED AS PRECIPITATES IN THIS PROCESS. HOWEVER, DUE TO THE PRESENCE OF CHELATING AND COMPLEXING AGENTS, INCOMPLETE REMOVALS OCCUR.

THE PILOT PLANT RESULTS REPORTED HERE WERE OBTAINED USING THE FINAL pH ADJUSTED EFFLUENT.

PILOT PLANT OPERATIONS

A SCHEMATIC OF THE REVERSE OSMOSIS SYSTEM IS ALSO SHOWN IN FIGURE 1.

THE CLARIFIED WASTE WATER WAS PUMPED TO A HOLDING AND EQUALIZATION TANK. DURING OPERATION WASTE WATER WAS PUMPED FROM THIS TANK THROUGH A MULTI-MEDIA PRESSURE FILTER. THE pH WAS FURTHER ADJUSTED TO 5 - 5.5 USING SULFURIC ACID AND POLYPHOSPHATE ADDED IN THE RANGE OF 10 MG/L TO AID IN CONTROL OF CALCIUM PRECIPITATION.

PRIOR TO ENTERING THE REVERSE OSMOSIS SYSTEM, THE WASTE WATER WAS PASSED THROUGH POLISHING CARTRIDGE FILTERS FOR REMOVAL OF PARTICLES LARGER THAN 10 MICRONS.

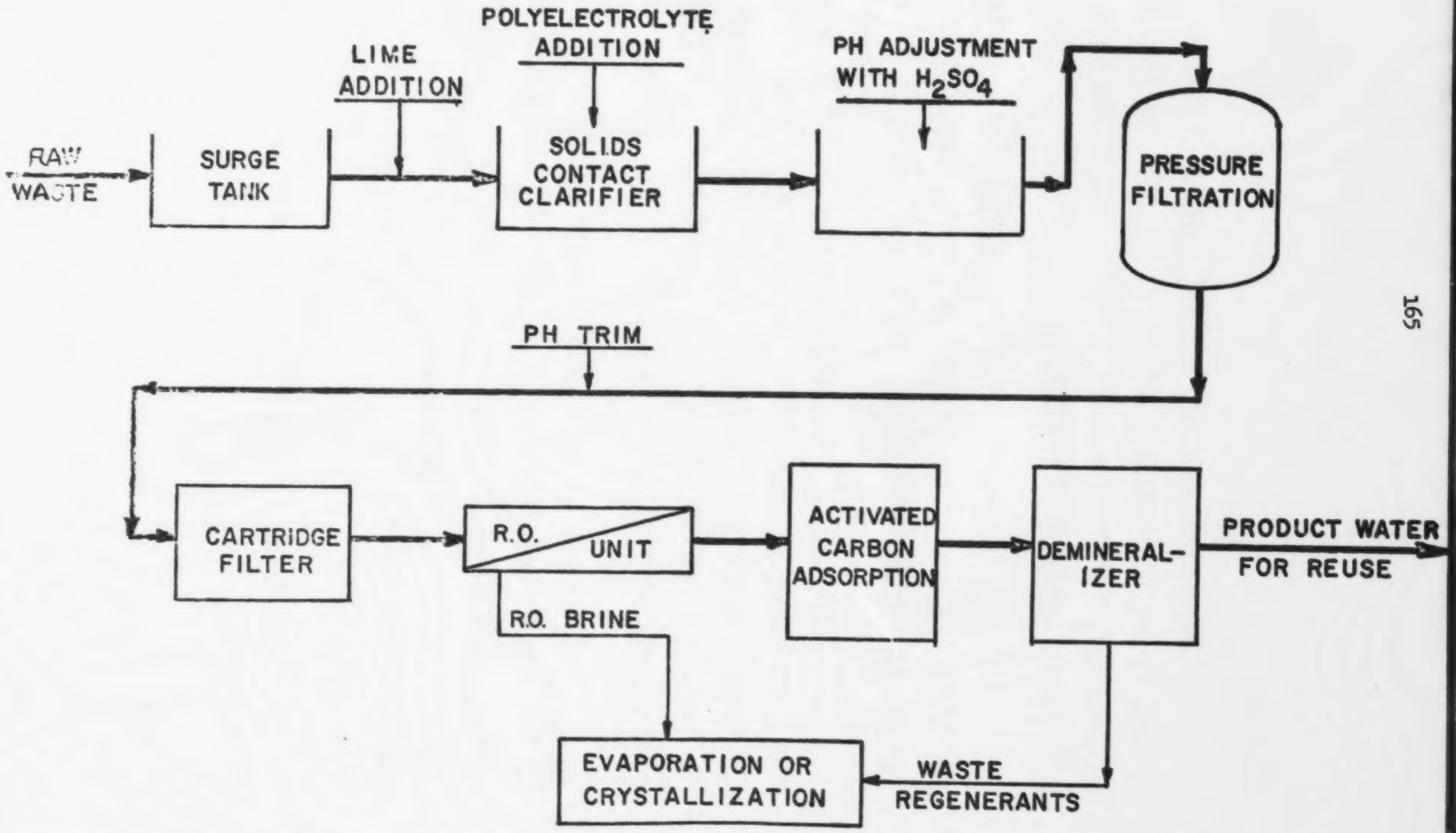
THE WASTE WATER WAS THEN PASSED THROUGH A REVERSE OSMOSIS SYSTEM CONSTRUCTED WITH ROGA MODEL 4100 SPIRAL-WOUND MODULES.

THE SYSTEM WAS OPERATED AT 75% RECOVERY.

OTHER PORTIONS OF THE PILOT PLANT PROGRAM INCLUDED THE EVALUATION OF ACTIVATED CARBON FOR REMOVAL OF TRACE ORGANIC COMPOUNDS, DEMINERALIZATION FOR THE PRODUCTION OF ULTRA-PURE WATER AND THE EVALUATION OF FREEZE CRYSTALLIZATION AND EVAPORATION FOR FINAL BRINE DISPOSAL. THESE PORTIONS ARE BEYOND THE SCOPE OF THE PRESENT PAPER.

FIGURE NO. 1

WASTE WATER TREATMENT FOR REUSE


RAW WASTE
SURGE TANK
LIME ADDITION
POLYELECTROLYTE ADDITION
SOLIDS CONTACT CLARIFIER
PH ADJUSTMENT WITH H_2SO_4
PRESSURE FILTRATION
PH TRIM
CARTRIDGE FILTER
R.O. UNIT
R.O. BRINE
ACTIVATED CARBON ADSORPTION
DEMINERAL- IZER
PRODUCT WATER FOR REUSE
WASTE REGENERANTS
EVAPORATION OR CRYSTALLIZATION

RESULTS

THE REVERSE OSMOSIS UNIT WAS STARTED ON MONDAYS AND ALLOWED TO RUN CONTINUOUSLY THROUGH FRIDAY. IN THE PERIOD REPORTED HERE COMPOSITE SAMPLES OF FEED, PRODUCT AND BRINE WERE TAKEN OVER 24-HOUR PERIODS.

DURING THIS PERIOD THE TOTAL DISSOLVED SOLIDS IN THE REVERSE OSMOSIS FEED RANGED FROM 2000 TO 4000 MG/L. AVERAGE SALT REJECTIONS RANGED FROM 93 TO 95 PERCENT.

FIGURE NO. 2 ILLUSTRATES THE FLUCTUATION OF TOTAL DISSOLVED SOLIDS BY CONDUCTIVITY IN THE REVERSE OSMOSIS FEED AND PRODUCT WATER. THE CONCENTRATION OF DISSOLVED SOLIDS IN THE PRODUCT WATER REMAINED RELATIVELY CONSTANT IN SPITE OF WIDE VARIATIONS IN FEED CONCENTRATIONS.

FIGURE NO. 3 ILLUSTRATES THE CONCENTRATION OF CALCIUM IN THE REVERSE OSMOSIS FEED FOR THE SAME PERIOD. CALCIUM CONCENTRATION HAS A MAJOR EFFECT ON THE DEGREE OF PRODUCT WATER RECOVERY WHICH CAN BE OBTAINED. IN THE PRESENCE OF SULFATES PRECIPITATION CAN OCCUR ON THE MEMBRANE SURFACES WHICH RESULTS IN A LOSS OF FLUX.

TABLE NO. 1 ILLUSTRATES HEAVY METAL REMOVALS DURING THIS PERIOD.

FIGURE 2

WEEKLY MEAN VALUES FOR CONDUCTIVITY
REVERSE OSMOSIS FEED AND PRODUCT

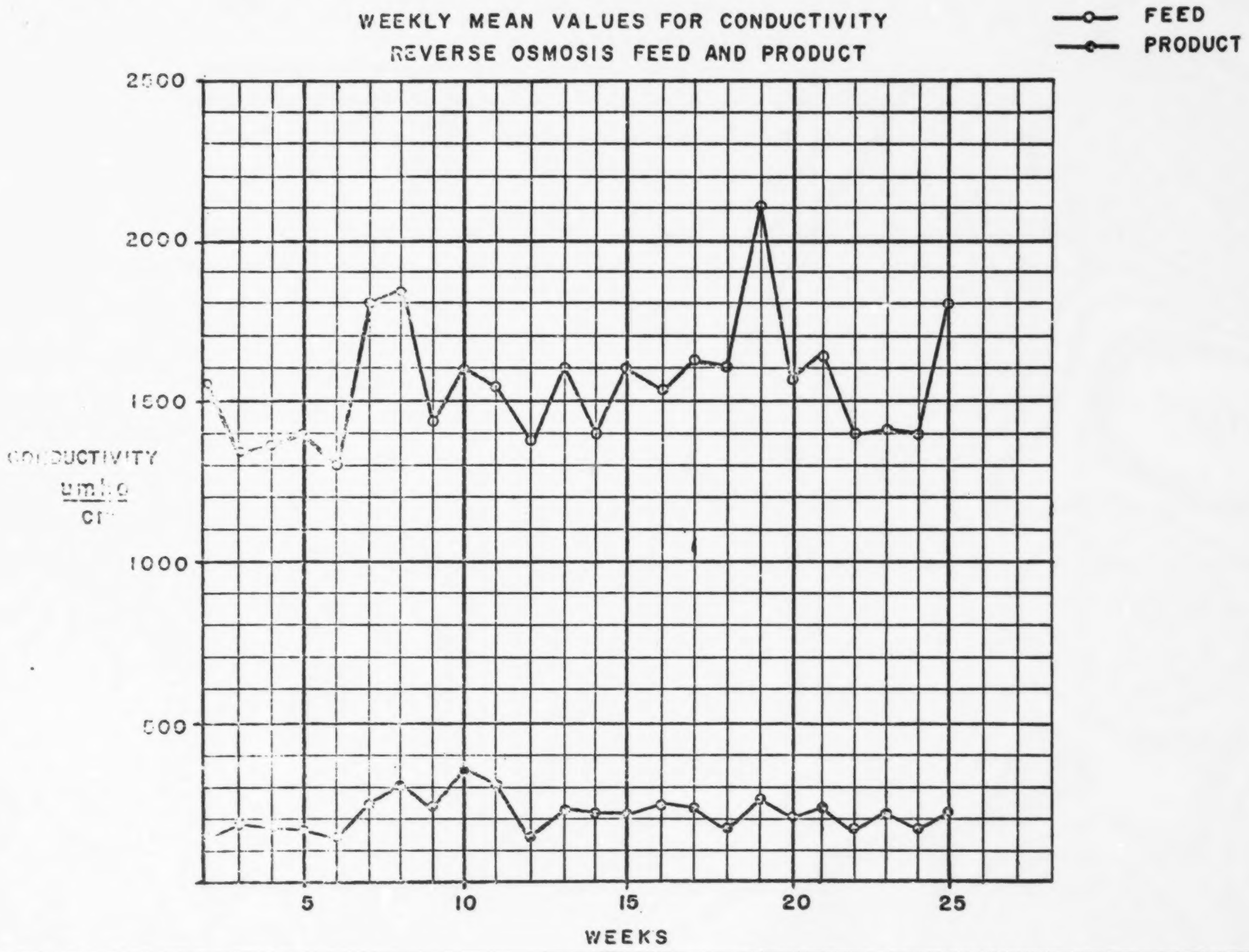


FIGURE 3

WEEKLY MEAN VALUES FOR CALCIUM
REVERSE OSMOSIS FEED

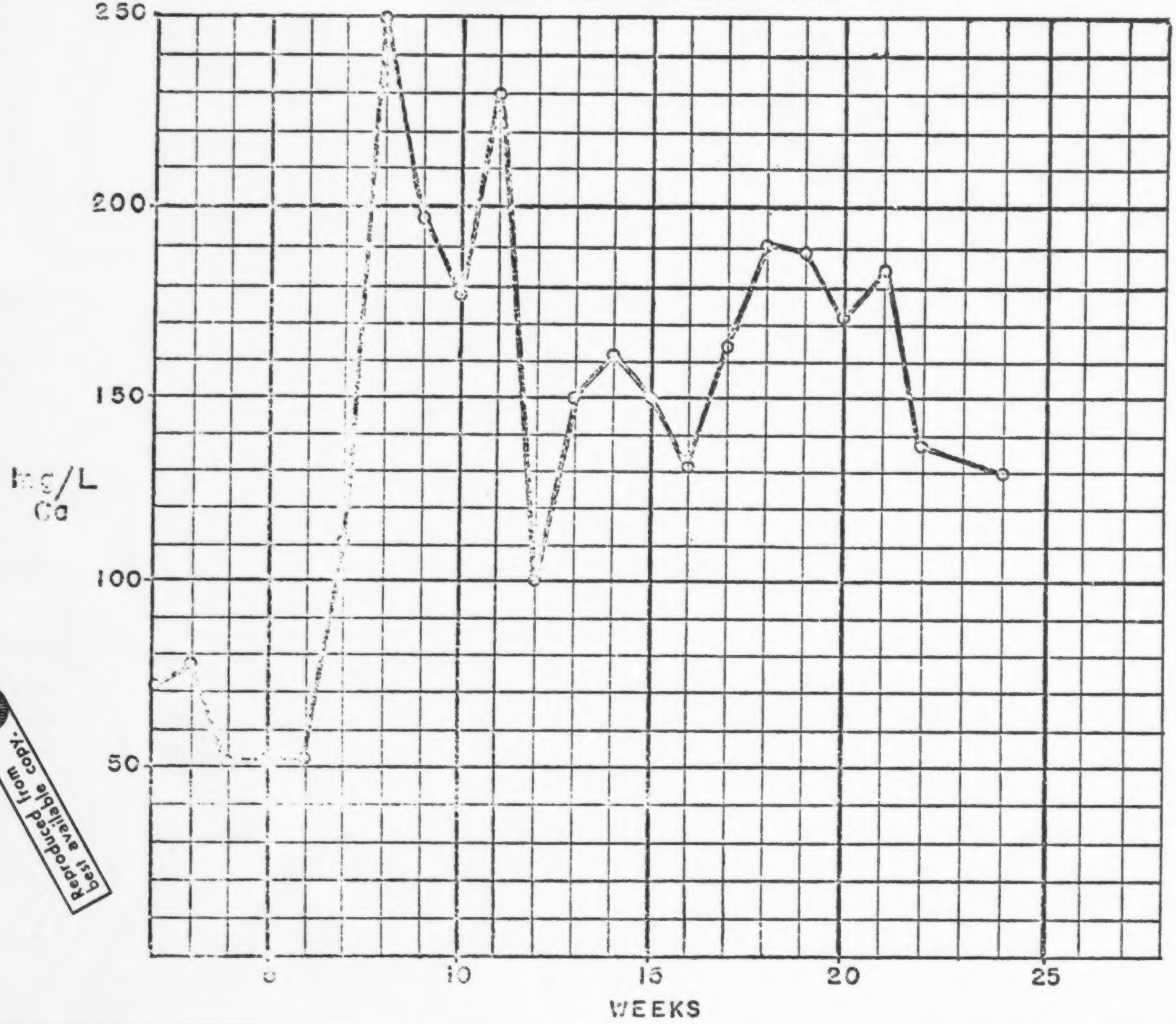


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TABLE 1
PERCENT METAL REMOVAL

METAL	AVERAGE REDUCTION - %	RANGE - %
Cd	66	43 - 83
Cr	82	73 - 90
Cu	98.6	97 - >99
Fe	94	92 - 98
Pb	>99	----
Zn	97	92 - >99
Ni	15	14 - 15

THE PERCENT REDUCTION OF COPPER, IRON, LEAD AND ZINC CORRESPOND ROUGHLY TO THE OVERALL REDUCTION IN TOTAL DISSOLVED SOLIDS. CADMIUM AND CHROME LEVELS INDICATE FAIR REMOVAL WHILE NICKEL LEVELS SHOWED VERY LITTLE REMOVAL.

TABLE NO. 2 GIVES THE CONCENTRATION OF HEAVY METALS IN THE REVERSE OSMOSIS FEED, PRODUCT AND BRINE FOR AN EIGHT WEEK PERIOD. DAILY RESULTS WERE AVERAGED FOR ONE WEEK PERIODS. ALL RESULTS ARE REPORTED AS MG/L OF THE METAL. ALL ANALYSES WERE PERFORMED BY ATOMIC ADSORPTION OR EMISSION SPECTROPHOTOMETRY.

CADMIUM LEVELS ARE QUITE LOW AND THE FAIR REDUCTIONS EXPERIENCED MAY BE A RESULT OF THE RESOLUTION OF THE MEASURING INSTRUMENTS.

TOTAL CHROMIUM LEVELS WERE RELATIVELY HIGHER THAN CADMIUM AND THE PRODUCT WATER CONCENTRATIONS LIKELY REFLECT THE LIMITATION OF THE SYSTEM. IN ALL CASES, HOWEVER, PRODUCT WATER CONTAINED LESS THAN 0.22 MG/L.

EXCELLENT COPPER REMOVALS WERE EXPERIENCED WITH PRODUCT WATER CONCENTRATIONS WELL BELOW THE ALLOWABLE 0.2 MG/L.

IRON REMOVALS WERE ALSO EXCELLENT WITH NO VALUES IN EXCESS OF 0.07 MG/L. LEAD WAS FOUND ONLY INFREQUENTLY. WHEN PRESENT HOWEVER IT WAS REMOVED TO BELOW DETECTABLE LIMITS. ZINC REMOVALS WERE ALSO EXCELLENT, AGAIN APPROACHING THE DETECTABLE LIMITS OF THE MEASURING LIMITS.

NICKEL LEVELS ALTHOUGH MEETING DISCHARGE REQUIREMENTS OF <1.0 MG/L SHOWED POOR REJECTION.

AT THE PRESENT TIME THE POSSIBILITY OF A NICKEL COMPLEX WITH SOME OF THE ORGANIC COMPOUNDS IN THE WASTEWATER IS BEING INVESTIGATED. NORMALLY NICKEL REJECTIONS ARE HIGHER THAN OUR TEST RESULTS INDICATED USUALLY IN THE RANGE OF >98 PERCENT.

TABLE NO. 2
METAL-ANALYSIS

	TOTAL						
	CD	CR	CU	FE	PB	ZN	NI
FEED	0.029	1.20	2.29	0.26	0.00	0.021	0.76
PRODUCT	0.011	0.22	0.07	0.02	0.00	0.005	0.61
BRINE	0.068	4.95	11.20	5.30	0.00	0.135	0.84
FEED	0.024	0.01	2.51	0.55	0.00	0.021	0.75
PRODUCT	0.009	0.15	0.04	0.02	0.00	0.00	0.59
BRINE	0.040	3.26	9.86	1.65	0.00	0.15	0.86

TABLE NO. 2 (CONT'D)
METAL ANALYSIS

	TOTAL						
	CD	CR	CU	FE	PB	ZN	NI
FEED	0.059	0.15	6.18	1.30	0.02	0.065	0.77
PRODUCT	0.010	0.02	0.07	0.07	0.00	0.001	0.66
BRINE	0.230	0.31	12.96	4.00	0.23	0.325	0.80
FEED	0.039	0.20	2.10	0.50	0.00	0.030	0.76
PRODUCT	0.011	0.02	0.06	0.04	0.00	0.002	0.66
BRINE	0.135	0.51	8.75	5.60	0.00	0.160	0.82

TABLE NO. 2 (CONT'D)
METAL ANALYSIS

	TOTAL						
	Cd	Cr	Cu	Fe	Pb	Zn	Ni
Feed	0.029	0.39	1.83	0.50	0.00	0.035	0.77
Product	0.011	0.07	0.00	0.04	0.00	0.000	0.65
Brine	0.060	1.10	6.34	2.40	0.00	0.160	0.77
Feed	0.032	1.03	3.17	0.70	0.00	0.035	0.74
Product	0.010	0.19	0.03	0.04	0.00	0.001	0.67
Brine	0.105	3.74	10.22	3.30	0.00	0.170	0.84

TABLE NO. 2.(CONT'D)
METAL ANALYSIS

	TOTAL						
	Cd	Cr	Cu	Fe	Pb	Zn	Ni
Feed	0.021	0.11	3.83	2.50	0.00	0.130	0.83
Product	0.012	0.03	0.03	0.06	0.00	0.010	0.70
Brine	0.069	0.22	12.23	5.25	0.00	0.960	1.05
Feed	0.040	0.13	5.90	1.00	0.025	0.085	0.82
Product	0.011	0.03	0.07	0.06	0.00	0.005	0.69
Brine	0.133	0.29	12.98	3.20	0.33	0.405	0.84

SUMMARY

AT THIS STAGE OF OUR INVESTIGATION WE HAVE DETERMINED THAT IT IS POSSIBLE TO PRODUCE A HIGH QUALITY WATER, LOW IN OVERALL HEAVY METAL CONTENT, FOR POSSIBLE RECYCLE IN PLANT MANUFACTURING OPERATIONS. THE ECONOMICS OF THE REVERSE OSMOSIS SYSTEM IS DIRECTLY RELATED TO THE PROJECTED LIFE OF THE MEMBRANES. THIS WILL BE DETERMINED BY TESTING INDIVIDUAL MODULES AT THE CONCLUSION OF THE STUDY.

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1. Revised Effluent Limitation Guidance for The Permit Program.
Metal Finishing Industry.
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2. Cruver, J. E., Reverse Osmosis for WATER USE
Conference on Complete Water Use, Washington D.C. April, 1973.

REMOVAL OF HEAVY METALS FROM WATER USING REVERSE OSMOSIS

by

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Princeton University Conference On

"Traces of Heavy Metals in Water:
Removal Processes & Monitoring"

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REMOVAL OF HEAVY METALS FROM WATER USING REVERSE OSMOSIS

by David H. Furukawa

Through the past decade, reverse osmosis has experienced a tremendous developmental effort which has taken it from a laboratory curiosity to commercial reality. Much of this work was sponsored by the Federal Government but several private companies were instrumental in finding commercial uses for the process through their own developmental efforts.

Although the controversy still exists on whether the transport phenomena related to reverse osmosis is explained by diffusion theory or pore flow theory, there is no doubt this membrane process has reached its place in industry as a unit operation.

In spite of extensive efforts to find better membrane materials, the predominant membrane used by the industry is still cellulose acetate or derivatives thereof. Although this polymer has outstanding transport characteristics, the use of this membrane is limited by several factors. Water transport changes considerably with feed water temperature. Water permeation generally increases approximately 2.5% per degree centigrade. The membrane is further limited by a maximum operating temperature of approximately 110° F.

The feed solution pH must be kept between the limits of 3.0 to 7.0 pH units with optimum being at approximately pH 5.5. Although membrane life of up to three years has been experienced at optimum pH, membrane life time is greatly deteriorated by high and low pH.

Obviously, osmotic pressure is a primary consideration in the degree of separation possible with this membrane process. Since most commercial reverse osmosis systems cannot be operated greater than 600 psi, concentration of inorganic ions is limited to a value which will have an osmotic pressure less than 600.

It is well known that reverse osmosis membranes exhibit extremely high rejection of heavy metals. The rejection of metals shown in Table 1 is a representative indication of membrane rejection. As the table shows, the rejection of heavy metals exceeds 99% in many cases. A factor which one must consider, however, in considering the use of reverse osmosis is that 100% of the fluid to be treated will come in contact with the membrane surface. The cost of the process therefore is more dependent upon quantity of water to be treated than quantity of heavy metal ions contained therein. The use of reverse osmosis must be considered on an economic basis as well as a technical separations basis. In most cases, reuse of the heavy metals removed must have significant value before the process can be economically used in a commercial operation. Fortunately, in many situations such by-product recovery and reuse is possible and realistic.

Another membrane technology closely related to reverse osmosis and often confused is ultrafiltration. The process is so named because of the use of membranes possessing much greater porosity than reverse osmosis membranes. With ultrafiltration membranes, the effects of osmotic pressures are minimized. The porous structure is such that inorganic ions are free to move through the membrane barrier. Separation of molecules is more dependent on molecular size and shape than molecular weight or valence. Ultrafiltration can play an important part in heavy metal recovery, particularly in those cases where the heavy metal ion can be easily complexed with an organic molecule of considerable size. The resulting organometallic compound may be of sufficient size to be excluded from the pores of the ultrafiltration membrane. Use of such membranes has significant value since ultrafiltration membranes generally have water transport characteristics which far exceed any of the reverse osmosis membranes and operate at lower pressure. An added advantage of ultrafiltration membranes is that several are available which tolerate greater extremes in pH than does cellulose acetate.

Considerable work has been performed (both academic and industrial) on the development of reverse osmosis for heavy metal removal.(1, 2)

The Fluid Sciences Division investigations with heavy metal removal began as early as 1968 when the company, which was then known as Havens International, began development of the process for concentration of a copper solution.(3) Even at this early date, it was quite obvious that the process had significant potential for use in heavy metal removal. It also became obvious that such metals must have considerable value for reuse before companies will be willing to approve significant capital expenditures for a new process. In these early tests a copper solution was concentrated from 1,130 ppm to 10,770 ppm representing nearly a ten-fold concentration. A significant portion of these early tests was spent in solving the problems related to membrane surface fouling.

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(1) "Application of Reverse Osmosis to Electroplating Waste Treatment, Part I Recovery of Nickel," by Golomb, A., Plating, October 1970

(2) "Reverse Osmosis Treatment of Diluted Nickel Plating Solutions," by Hauck, Andrew R. and Sourirajan, S., Journal WPCF, Volume 44, No. 7, July 1972

(3) "Applications of Reverse Osmosis for Concentration of Copper Leaching Liquor," by Guy, D. B. and Lindsay, A.K., Havens Industries, San Diego, California, February 21, 1968, Internal Report

In late 1968, tests were begun in Great Britain using Fluid Sciences (formerly Havens International) membranes to recover nickel. (4) Water was taken from the counter-flow rinsing tanks for concentration by reverse osmosis with product water returned to the rinsing process. The concentrated nickel was then returned to the plating bath. This process has since been used successfully by others. (5) An overall 98% nickel recovery was achieved with 90% water recovery.

A more recent developmental effort has been initiated in use of reverse osmosis as one step necessary to convert a pyrolytic nickel process to a hydro-metallurgic process. Reverse osmosis is used for concentration of the nickel stream prior to final recovery. This application is in a very early developmental period and commercial application may not be realized for many months.

In all of the application areas investigated thus far by Fluid Sciences, the metals recovered from the waste or process streams have considerable value in reuse. In these situations the use of reverse osmosis pays handsome dividends in savings.

In most applications for reverse osmosis and heavy metal recovery, potential problem areas exist. The most common phenomenon which must be considered is concentration polarization. This phenomenon results in much higher concentration of the metal salts at the membrane surface than would be normally found in the bulk solution. In order to minimize these effects, it is important to establish fully turbulent flow to reduce the boundary layer thickness.

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(4) "Nickel Recovery by Reverse Osmosis," Havens International, San Diego, California, November 28, 1969, Internal Communication

(5) "Reverse Osmosis for Reclamation and Reuse of Chemical and Metal Waste Solutions," by Spatz, D. Dean, Osmonics Inc., Minneapolis, Minnesota, December 1, 1970

Membrane fouling is another problem area. Since the degree of membrane fouling will increase as salts are carried toward the membrane by convection, it is important to control the degree of membrane permeation as well as velocity within the flow channel.

Other factors such as membrane compaction and system configuration have been well discussed in literature. These considerations are common to the process and not particularly unique to heavy metal removal.

In general, the strongest incentive to use reverse osmosis is economics. In addition to the economics afforded by valuable by-product recovery, reverse osmosis offers a concentration step that is uniquely more economic than conventional methods such as evaporation. The only energy consumed by the process is pumping energy. The thermal energy input required by evaporation is not necessary with reverse osmosis. Because the process has not been widely used, accurate economic data on full sized commercial systems is not available.

The greatest advances in the reverse osmosis process will probably come in the area of membrane development. Most companies actively engaged in the manufacture of reverse osmosis equipment are pursuing membranes made of polymers other than cellulose acetate. A cellulose acetate polymer, although excellent for many applications, has limitations in pH (3 to 7), temperature (approximately 110° F), and resistance to various solvents. One of the most successful new membranes has been developed by North Star Research & Development Institute, Minneapolis, Minnesota.(6, 7) The

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(6) "NS-1 Membranes for Reverse Osmosis," by Rozelle, L.T., Cadotte, J.E., and Kopp, C.V., North Star Research & Development Institute, Minneapolis, Minnesota 55406

(7) "Ultrathin Membranes for Treatment of Waste Effluents by Reverse Osmosis," by Rozelle, L.T., Cadotte, J.E., Nelson, B.R., and Kopp, C.V., North Star Research & Development Institute, Minneapolis, Minnesota 55406

North Star polymer membrane, known as the NS-1 membrane, is a non-polysaccharide membrane. The membrane consists of a polyethylenimine-coated microporous support (polysulfone) treated with m-tolylene-2-4-diisocyanate. This membrane has exhibited excellent product water flux (equal or better than cellulose acetate), and has resistance to pH from less than 1 up to 13. Typical copper ion rejection is 99.8%. This membrane shows great promise as a second generation membrane.

Fluid Sciences Division has undertaken further development of the NS-1 membrane in tubular form using existing membrane support tubes. The Fluid Sciences' proprietary tubular design provides an excellent substrate for this new membrane. Although the formulations are slightly different, the basic characteristics of the tubular membrane are very similar to the North Star formulation. Samples of this new tubular membrane, when tested and compared to cellulose acetate, were found to possess much higher rejection of organic compounds as well as higher rejection of most inorganic salts.

The reverse osmosis process is now widely used in many commercial applications. It should be strongly considered as a unit operation to be used in concert with other established unit operations common to industry. The process, although unique and attractive, may not solve a problem in total; however, combination with other processes provides a most attractive package for both waste water treatment and inline processing.

TABLE 1

REJECTION OF METAL SALTS BY REVERSE OSMOSIS MEMBRANES

	Typical Rejection Percent
Iron	99
Magnesium	98
Copper	99
Nickel	99.2
Chromium, Hexavalent	97.8
Strontium	99
Cadmium	98
Silver	96
Aluminum	99

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uop

February 1, 1974

CELLULOSE ACETATE MEMBRANES AND THEIR SELECTIVITY

Membrane Code	Test Pressure "P" p.s.i.g.	Water Flux at "P" and 25°C (Mean) G.F.S.D.	% Rejection of 0.45% NaCl	% Rejection of 6% Sucrose	% Rejection of 2.5% 6K P.E.G. Av. M.W. 6500	% Rejection of 2.5% 20K P.E.G.	% Rejection of 2.5% P.V.P. 30K Av. M.W. 40,000	Limiting Operational Conditions		
								Feed Temperature °C	Maximum Pressure p.s.i.g.	Feed pH Range
720	700	9	98.5-99.5	-	-	-	-	15-38	700	3-7
								38-50	600	4-6
620	600	14	97-98.5	-	-	-	-	15-38	700	3-7
								38-50	600	4-6
520	600	18	95-97	-	-	-	-	15-38	650	3-7
								38-50	550	4-6
420	600	23	89-93	97-98	-	-	-	15-38	600	3-7
								38-50	500	4-6
370	600	28	80-85	95-97	-	-	-	15-25	600	3-7
								25-35	500	4-6
320	500	30	65-75	93-95	98-99	> 99	-	15-25	600	3-7
								25-35	500	4-6
220	150	30-40	-	< 5	30-40	90-95	95-98	15-40	250	2.5-8.0
								40-55	150	3-7
225	150	25-35	-	< 5	10-20	90-95	95-98	15-40	250	1.5-11.0
								40-55	150	2-10
215	150	35-45	-	< 5	10	80-88	90-95	15-35	200	2.5-8.0
								35-45	150	3-7

FOAM AND BUBBLE FRACTIONATION FOR REMOVAL OF TRACE METAL IONS FROM WATER*

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Comparison of Processes

The selection of candidate separation processes for a given application can often be based upon an identification of certain salient features of the application, followed by matching these features with factors which are known to favor one separation process over others (King, 1971). The most striking feature of the problem of trace metals removal is the very high dilution of the substance to be removed. Another feature is the ionic character of that substance.

Because of the high dilution one is led to seek processes which remove the ions from the water into another phase or stream, rather than processes which remove the water. This places processes such as evaporation and freezing at a disadvantage. As we have seen in other papers presented at this conference, these processes which concentrate the feed by removing water should be considered for use only after the metal ions have been brought up to a minimum level of concentration by some other process. Thus processes removing the water are suitable only for very concentrated feeds or as the last stage of a process which also uses other separations.

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* Presented at Environmental Protection Agency Conference on Traces of Metals in Water, Removal and Monitoring, Princeton, N.J. November 16, 1973.

Among processes which remove the ions from the water, ones will be favored which somehow derive an economic advantage from the low level of concentration of the ions. Consider, for example, an extraction process, such as the use of liquid ion exchangers (Lewis, 1973; Agers and DeMent, 1972) to remove the metal ions into an organic phase. In these processes the distribution coefficient for the metal ion between phases tends to be insensitive to the concentration of the ion, at least beyond a sufficient level of dilution. Therefore the amount of solvent circulation per unit of water feed required to carry out the process does not change significantly as the metal ion becomes more dilute. As a consequence the process operating cost is relatively insensitive to the metal ion concentration.

On the other hand, fixed-bed processes such as adsorption and ion exchange with a solid resin do derive an advantage from a lower concentration of the substance being removed. The frequency of regeneration required for the solid phase and amount of regenerant required are inversely proportional to the feed concentration, since the solid phase will have a fixed uptake capacity. Thus it is no accident that ion exchange with solid resins has been one of the most successful processes for the removal of heavy metal ions at high dilution from water.

As a generalization of the processes removing the ions from the water, ion exchange and adsorption processes will be relatively favored for very dilute feeds (say below 20 ppm), whereas extraction with liquid ion exchangers is relatively favored for higher-concentration feeds.

Another process capable of removing some metal ions - e.g., copper - selectively from effluent waters is electrochemical reduction (Bennion and Newman, 1972; Posey, 1973). Here the current requirement per unit of feed becomes less for lower feed concentration; however competing reactions and the economics associated with non-separative electrical potential loss make this approach appear to be more promising for feed concentrations of intermediate level.

Foam and Bubble Fractionation

Foam fractionation and bubble fractionation are separation processes based upon the selective adsorption of surface-active species at a gas-liquid interface. By generating large quantities of interface and removing it in an appropriate way one can then effect a separation of species which are surface-active from those that are not. Foam and bubble fractionation are particularly well-suited for the removal of surface-active substances present at high dilution, since the amount of surface which can be generated per unit time is limited, since the selectivity of adsorption of surface-active species is often extremely high, and since surface-adsorption isotherms are usually highly non-linear. These factors interact to give a rapid increase in distribution coefficient as the level of concentration becomes lower. Foam and bubble fractionation are capable of providing heavy metal ion removal through selective attraction of counter-ions to anionic surfactant molecules, or by chelation or other specific interactions with surface-active species. Consequently foam and bubble fractionation are strong contenders for the removal of heavy metal ions present at high dilution, say below 10 ppm. In some situations they can be attractive for feeds of even higher concentration.

Foam fractionation for the removal and concentration of ions from solution has received a considerable amount of attention (Rubin and Gaden, 1962; Dick and Talbot, 1971; Lemlich, 1972; Somasundaran, 1972), with the principal intended application having been the decontamination of radioactive waste waters. In some cases separations have also been demonstrated on a pilot scale (Haas and Johnson, 1965; Arod, 1968).

Background of the Present Work

The work reported in this paper has been concerned with the removal of surfactants and copper from the effluent blowdown brine of evaporation seawater desalination plants. The research has been carried out in connection with the development of a process using surface-active agents to enhance the heat-transfer coefficient and reduce the pressure drop in vertical-tube, upflow evaporation (Sephton, 1971). Foam and bubble fractionation are used to recover and remove the surfactant from the effluent brine. The removal of copper is also of importance since copper enters the water through corrosion and is at a level (about 0.5 ppm) high enough so that it may be deleterious to marine life if the brine is returned directly to the ocean.

Foam and bubble fractionation experiments have been carried out in apparatus of various sizes, including (1) a 2-1/2 in. diameter, 6-ft high column, (2) a 1-ft square, 7-ft high column, and (3) a 4-ft square x 9-ft high chamber. Data obtained with the smaller column are reported here. Results for surfactant removal with the 1-ft square column are reported elsewhere (Valdes-Krieg, et al, 1974).

The surfactant employed has been Neodol 25-3A (Shell Chemical Co.), which is the ammonium salt of a sulfated primary alcohol with three ethylene oxide units and a C_{12} to C_{15} alkyl group.

Equilibrium Data

As is noted in the paper by Lemlich at this Conference, the surface enrichment of a surface-active species can be estimated from surface-tension data by use of the Gibbs adsorption isotherm, although some critical assumptions are often necessary. Surface enrichments calculated in this way from surface-tension data of Neodol in fresh water, normal seawater (Bodega, California), doubly concentrated and triply concentrated seawater are shown in Fig. 1. The surface excess concentration, $\mu g/cm^2$, is normalized by the bubble diameter, cm, with the bubble diameter assumed to be 0.1 cm. Equilibrium data are presented in this way since it is the ratio Γ/d which is found from experimental measurements where a foam fraction is collected and the volumetric air flow rate is known. Since the surface-to-volume ratio for spherical bubbles is 6/d, the

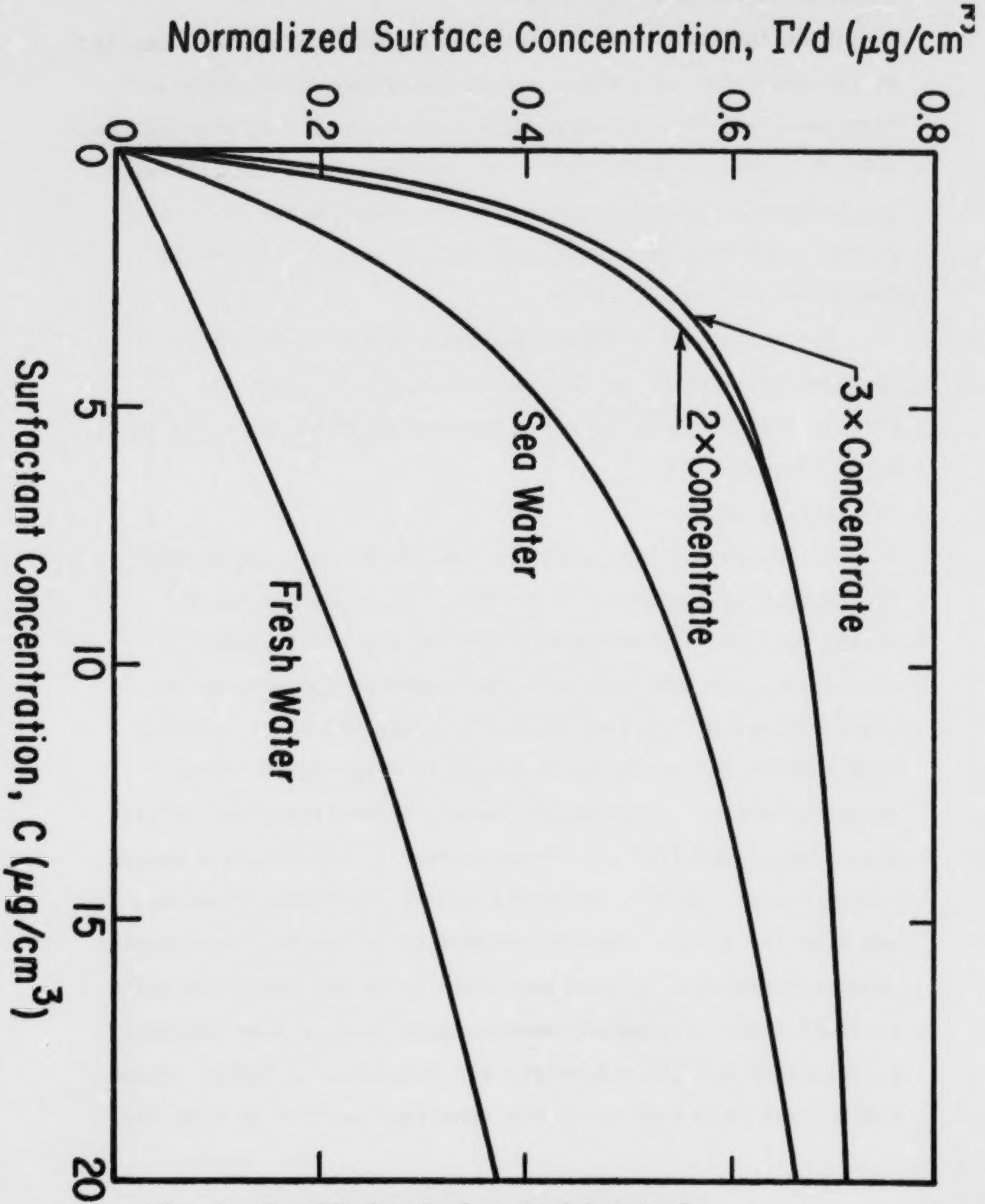

Fig. 1. Equilibrium Surface Enrichments for Neodol Calculated from Surface-Tension Data.

value of Γ/d may be thought of as one-sixth of the surfactant content of the foam per unit volume of air; however the liquid entrained with the foam is also important and sometimes dominant. The rate of change of surface concentration with increasing bulk concentration of the surfactant becomes less as the bulk concentration increases and the surface becomes more saturated, resulting in lower equilibrium distribution coefficients between surface and bulk at higher surfactant concentrations. Note also that the surface concentration is greater and levels off at a lower bulk surfactant content in seawater than in fresh water. This is the result of the ionic content displacing the surfactant towards the interface in seawater.

It is preferable for metals removal to limit surfactant concentrations to those where there is still an appreciable slope in Fig. 1, so as to allow for easier removal of the surfactant itself by foam fractionation. In the present work low surfactant concentrations have also been of interest since the most economical heat-transfer enhancement effect in seawater evaporators is realized at surfactant concentrations of about 10 ppm (Sephton, 1973). This is substantially lower than the sodium lauryl sulfate concentrations of 200 to 400 ppm which have been used by others for copper removal (Dick and Talbot, 1971).

Figure 2 shows results of experimental measurements of equilibrium surface enrichments for Neodol in a synthetic triply-concentrated seawater brine (10.5 wt % NaCl). The

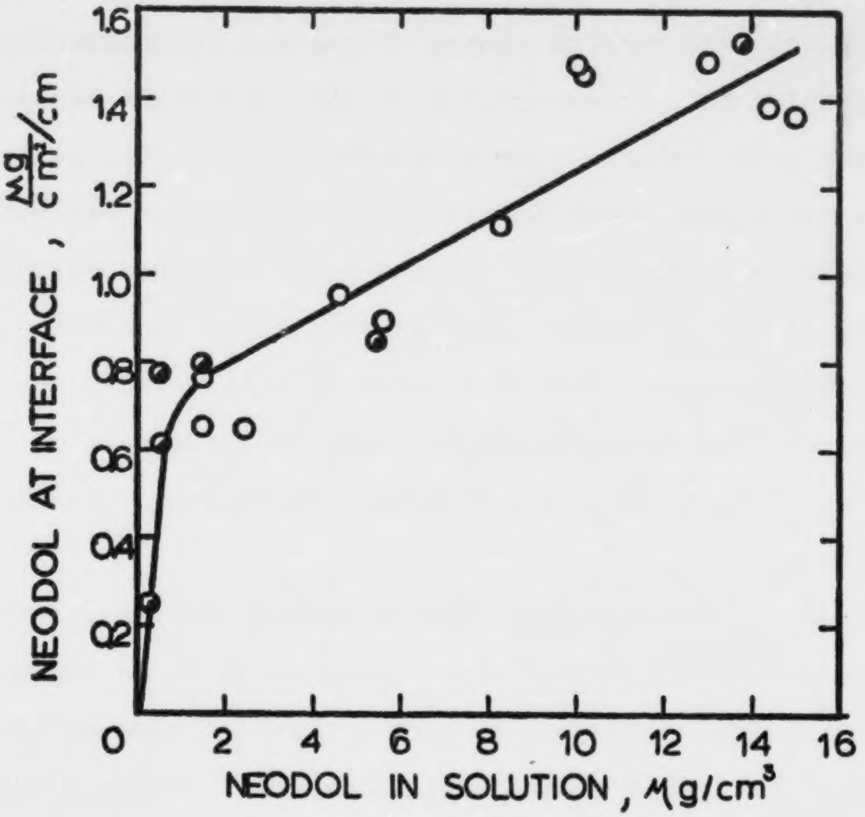

Fig. 2. Equilibrium Surface Concentration of Neodol (Γ/d) in 10.5% NaCl Solution.

open points were determined by sampling the foam immediately above and the liquid immediately below an interface between a relatively non-draining foam region and a liquid-continuous bubble region in a foam and bubble fractionation column of the sort shown in Figure 3. The half-shaded points were obtained by a technique using concurrent flow of liquid and air (liquid feed near the bottom of the column), coupled with measurement of the depletion of surfactant content of the liquid along the direction of flow. This latter technique is suitable for very low surfactant concentrations where foam coalescence is substantial.

Figure 4 shows equilibrium surface enrichments of copper ion in otherwise pure water containing 34.8 ppm of Neodol, for which Γ/d for Neodol is 1.23 $\mu g/cm^3$. These data were obtained by means of the concurrent flow technique. It is apparent that substantial surface enrichments of copper are possible, even at this rather low surfactant content.

Foam Column Operation

Figure 3 shows a schematic of a column as used for combined foam and bubble fractionation in most of this work. Air is supplied through a porous fused-silica diffuser plate (10μm nominal pore size, Filtros Co.) at the bottom, in the form of fine bubbles. Although the liquid-continuous bottom (bubble) section has frequently been considered as a well-mixed single stage, it has been found in the present work that substantial separations can be accomplished by operating

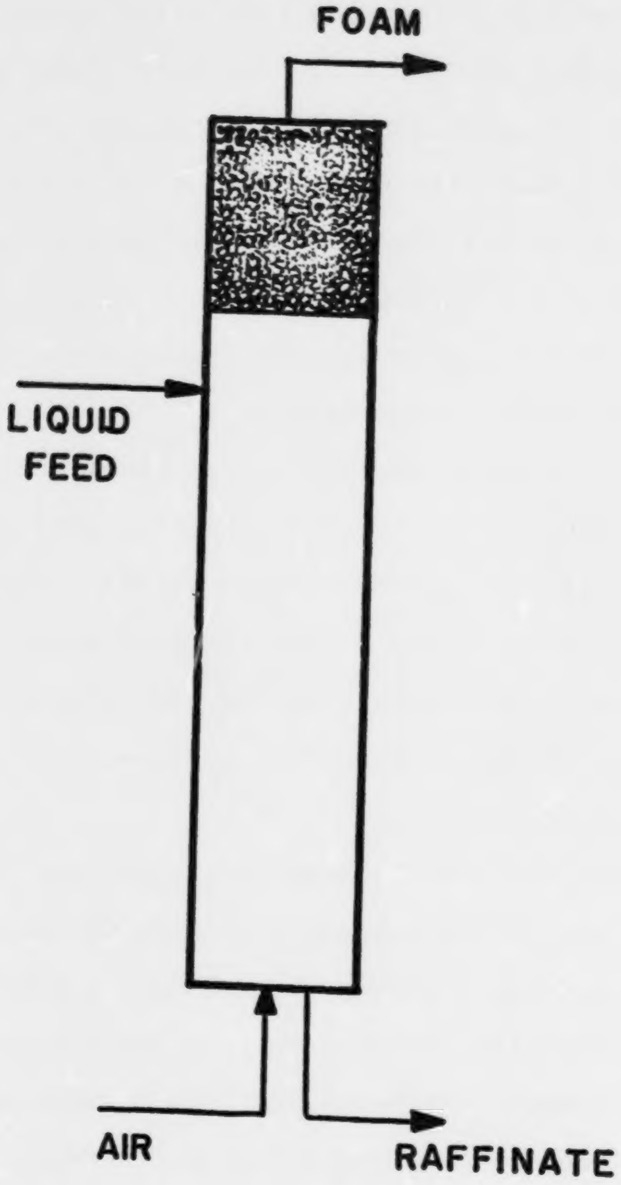
FOAM
LIQUID FEED
AIR
RAFFINATE

Fig. 3. Schematic of a Simple Column for Foam and Bubble Fractionation.

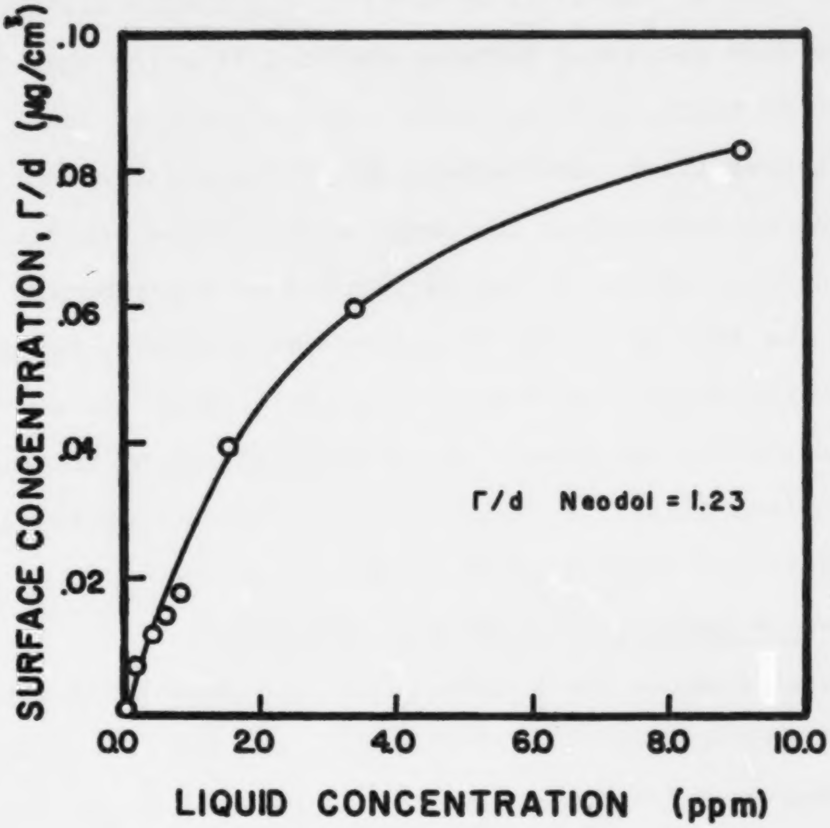

Fig. 4. Equilibrium Surface Concentration of Copper in Otherwise Pure Water containing 34.8 ppm Neodol.

this section with minimal axial mixing. Hence the bubble region occupies most of the column height. The foam section is long enough to allow the removal of entrained liquid by drainage from the upflowing foamate product.

The liquid feed is introduced to the bubble section rather than the foam section. Putting the feed into the foam section can provide higher mass-transfer rates and can in some circumstances allow simultaneous multi-stage enrichment and stripping of surfactants and metal ions. These beneficial aspects can be offset by the difficulty of distributing the feed in the foam so as not to cause foam breakage, by the inherent instability of foams - especially with low surfactant contents - which can result in channeling, and by the much larger column diameters which would be required by the low liquid drainage rates typical of most foams.

Simultaneous Removal of Surfactant and Copper

Figure 5 shows the % removal of both Neodol and copper obtained from a feed of 10.5 wt % NaCl solution containing 24 ppm Neodol and 0.6 ppm copper in solution. The experiments were carried out with a bubble section height of 5 ft and a foam section height of 1 ft in the 2-1/2 in. diameter column, with about 10% of the feed removed as foamate. The removal is shown as a function of the volumetric air-to-water feed ratio, which was varied by changing the feed flow while holding the air flow constant at 1500 cm^3/min. The surfactant removal capability is proportional to the rate of interface

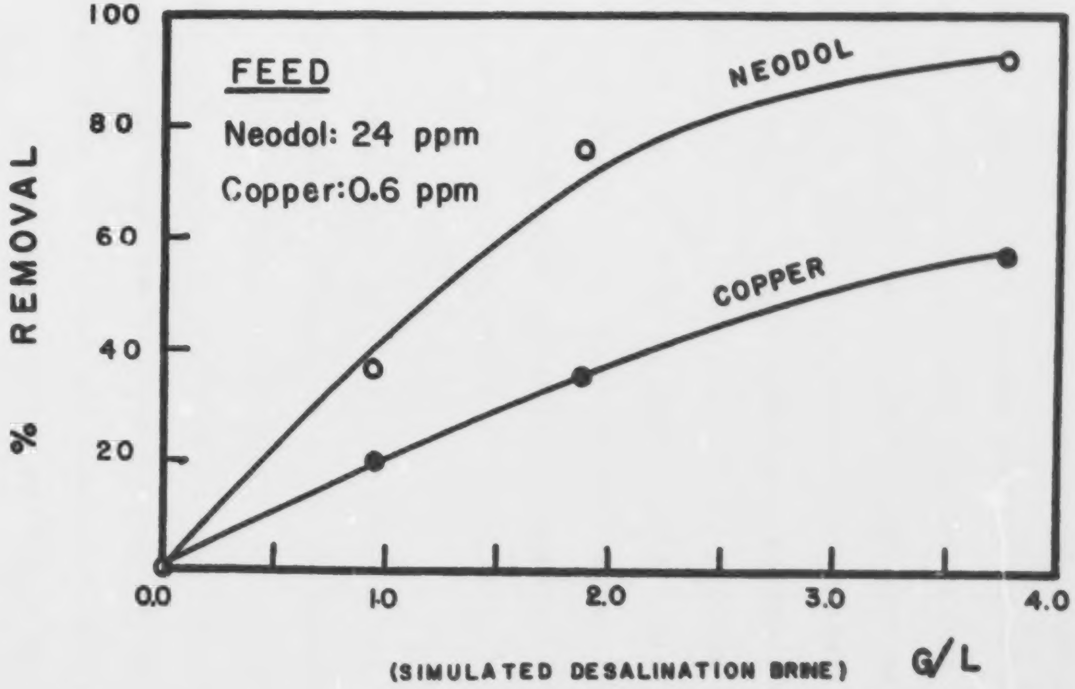

Fig. 5. Effect of Volumetric Air-to-Water Flow on Simultaneous Removal of Neodol and Copper from 10.5 wt % NaCl Solution.

generation, which in turn is proportional to the air flow rate. The removal increases as G/L increases since a lower liquid flow results in a lesser volume of liquid treated by a given surfactant removal capacity from the air flow. The G/L ratios used here are lower than in most previous foam and bubble fractionation applications.

Figure 6 shows removals of Neodol and copper at a fixed G/L, but at varying feed concentrations of Neodol. The results differ from the corresponding point in Figure 5 because of a different column overhead design resulting in different foam breakage characteristics. Surfactant recoveries are high as long as the surfactant concentration is high enough to yield a stable foam to carry it out the top of the column. Copper recoveries increase with increasing feed surfactant concentrations, as would be expected since the capacity of the surface for copper should increase as the surfactant content increases.

It is important to note from these results that, although the copper recoveries are substantially below 100%, the selectivity of the surface for copper ion is extremely high. Sodium is present in the solution at a concentration of 10^3 ppm, and yet is not appreciably enriched in the surface phase.

Figure 7 shows the results of axial sampling of the bubble section along its height during a run. There is a very considerable gradient in Neodol liquid-phase concentration along the column, which is a major contributor to the very high recoveries of Neodol shown in Figures 5 and 6. This gradient is the natural result of stripping of the Neodol from the

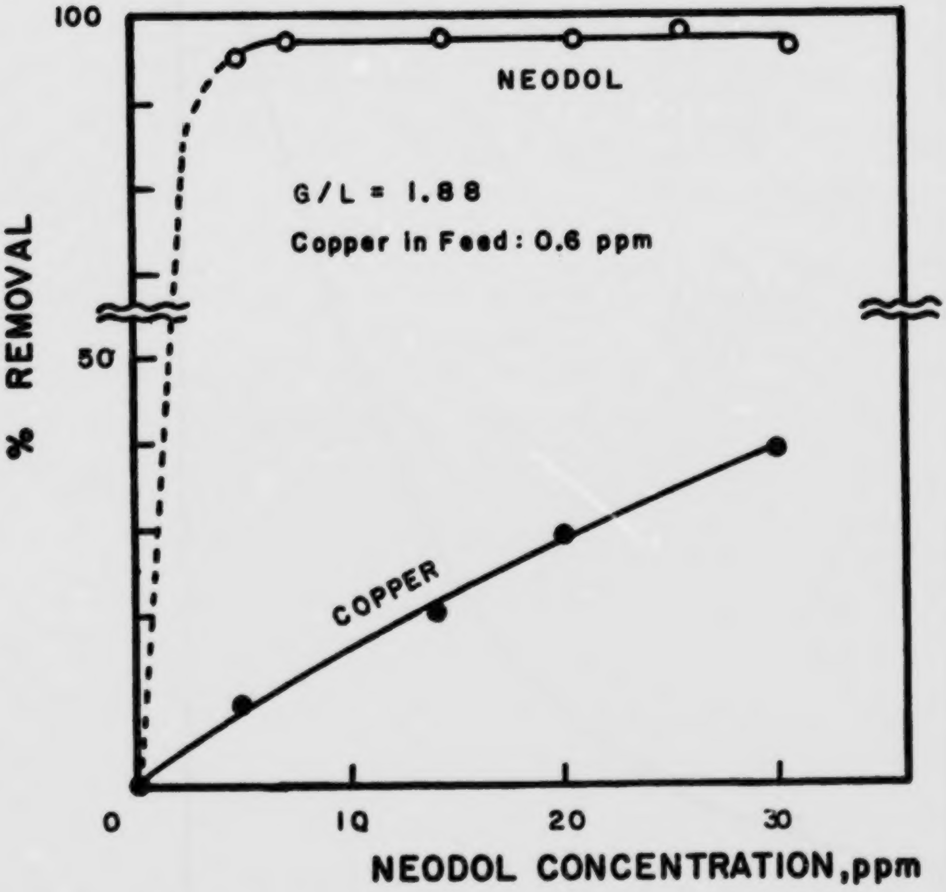

Fig. 6. Simultaneous Effect of Feed Neodol Concentration on Removal of Neodol and Copper from 10.5 wt % NaCl Solution.

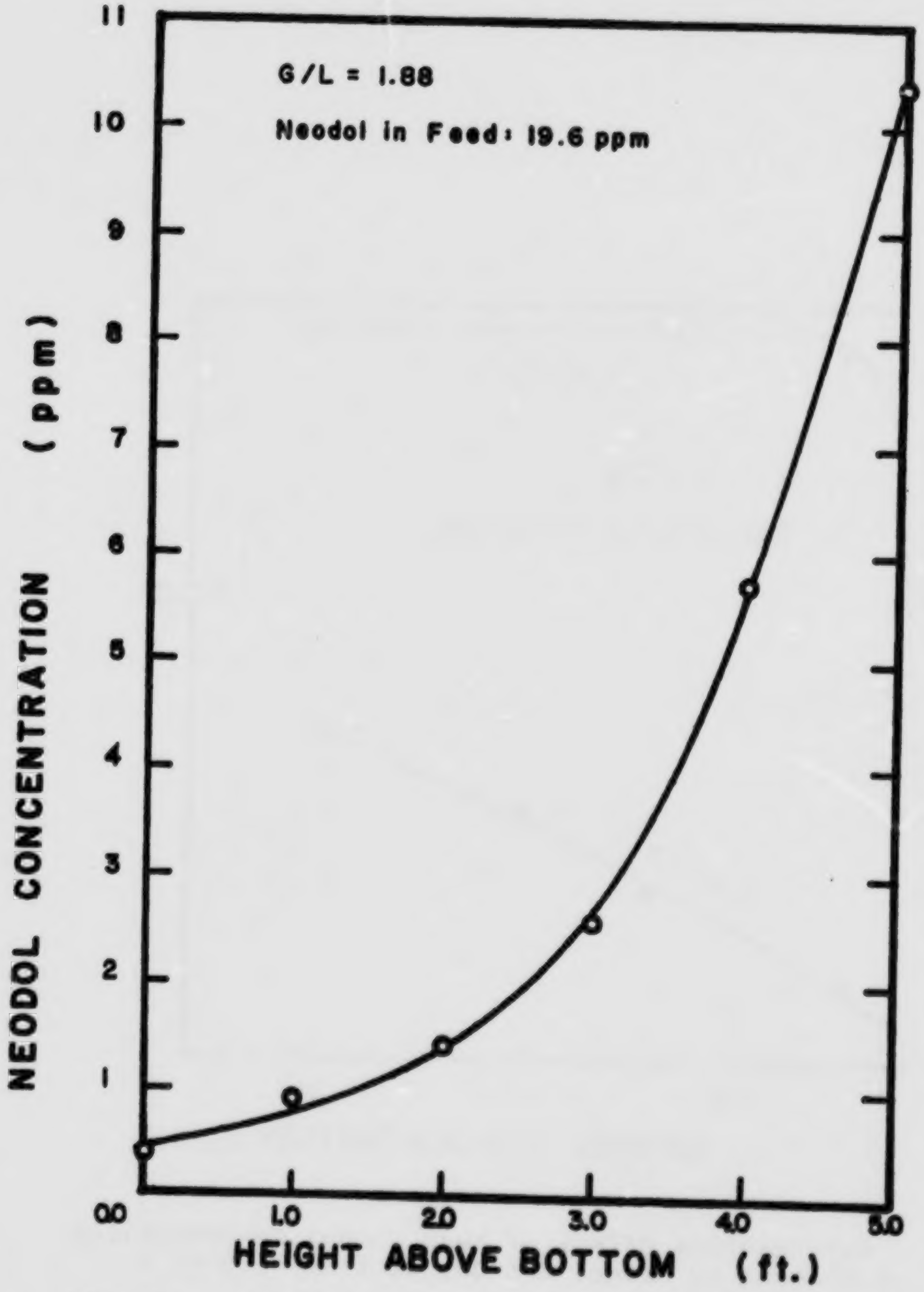

Fig. 7. Axial Concentration Profile for Neodol in Bubble Section; 10.5 wt % NaCl Solution.

downflowing liquid by the rising gas bubbles, and exists to the extent that it is not eliminated by large-scale bulk motions causing axial mixing within the bubble section. Note also that the liquid surfactant concentration at the feed location is substantially less than the concentration in the feed itself. This is a result of partial axial mixing, which dilutes the feed with bulk liquid brought up from lower in the column.

An axial concentration profile for copper obtained in the same run is shown in Figure 8. Again there is a substantial drop in concentration between the feed copper content (dark circle) and the concentration in the liquid phase at the feed location. This is again indicative of dilution of the feed by axial mixing with liquid from lower in the column. It is also striking to note that the copper concentration profile does not show the same gradient evidenced by the Neodol concentration; in fact the copper profile is essentially flat. Whereas much of the depletion of the water raffinate in Neodol is accomplished by bubble fractionation in the liquid section, the copper removal is accomplished almost solely by the enrichment of copper into the foam occurring at the interface between the bubble section and the foam section.

This different axial profile for copper and the lower % removals for copper than for Neodol are accounted for by the depletion of Neodol in the liquid phase proceeding down the column. Lower Neodol concentrations give a lower equilibrium distribution coefficient for the copper between surface and bulk. The gradient in copper concentration, to the extent that

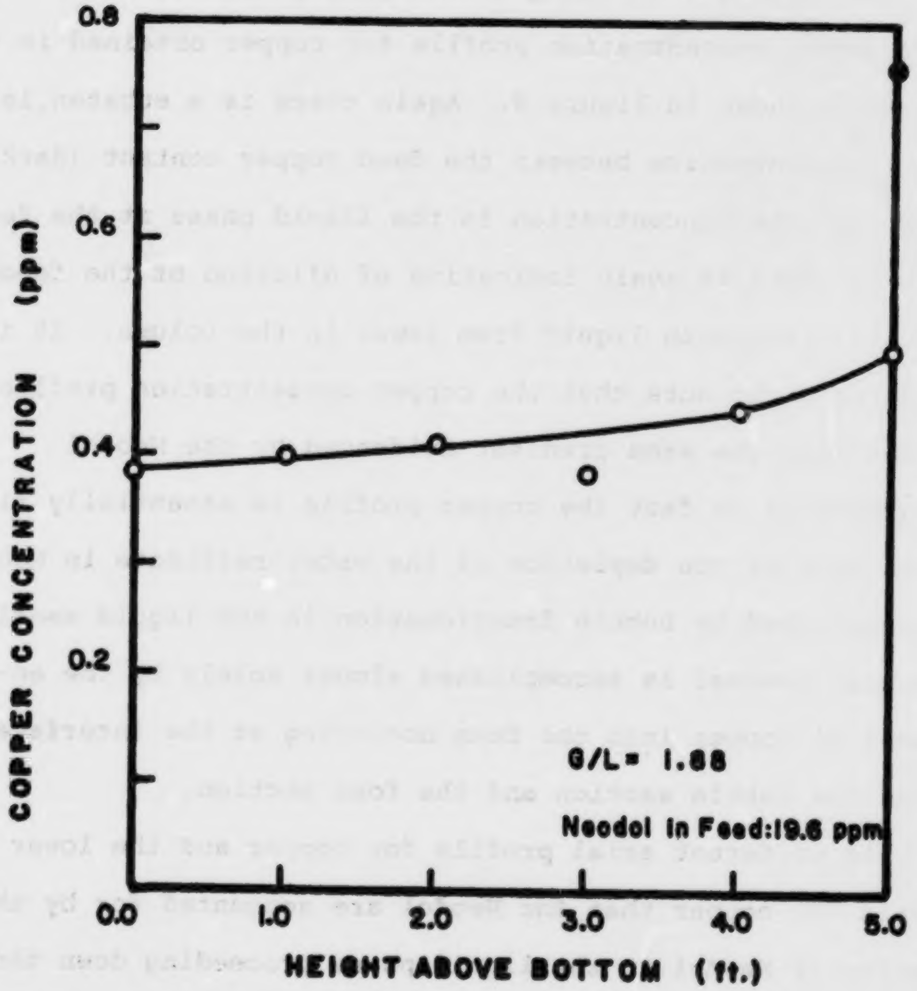

Fig. 8. Axial Concentration Profile for Copper in Bubble Section; Simultaneous Removal of Neodol and Copper; 10.5 wt % NaCl Solution.

it is present in Figure 8, occurs in that region of the column where the Neodol content is still relatively high. Lower in the bubble section the copper distribution coefficient must be less, so that the stripping factor, 6 $\Gamma G/Ld$, is reduced. This precludes effective stripping of the copper because of the limited capacity of the upflowing surface.

Improved Method for Removing Copper

Surfactant concentrations throughout the bubble section can be increased by feeding a surfactant-rich stream near the bottom of the column. Then, even if the surfactant is readily removed into the foam, there must be a significant surfactant concentration all along the liquid because of the necessity of an upward surfactant flux at all levels of the column.

The results of such an operation are shown in Figure 9. Over 99% of the copper is removed from a feed containing 1.0 ppm copper in the form of $CuSO_4$ in an otherwise pure water stream. Neodol is fed both at the lower feed and the main feed. A larger (4-1/2 in) diameter section is used as a portion of the foam section to allow adequate foam drainage at the high surfactant content. It is anticipated that the process could work as well without the Neodol being present in the upper feed, and that good copper recoveries could be obtained with even smaller amounts of surfactant being present. Even in the operation shown the surfactant concentrations are substantially lower than those which have been used elsewhere for metals removal by foam fractionation, with the feed entering a

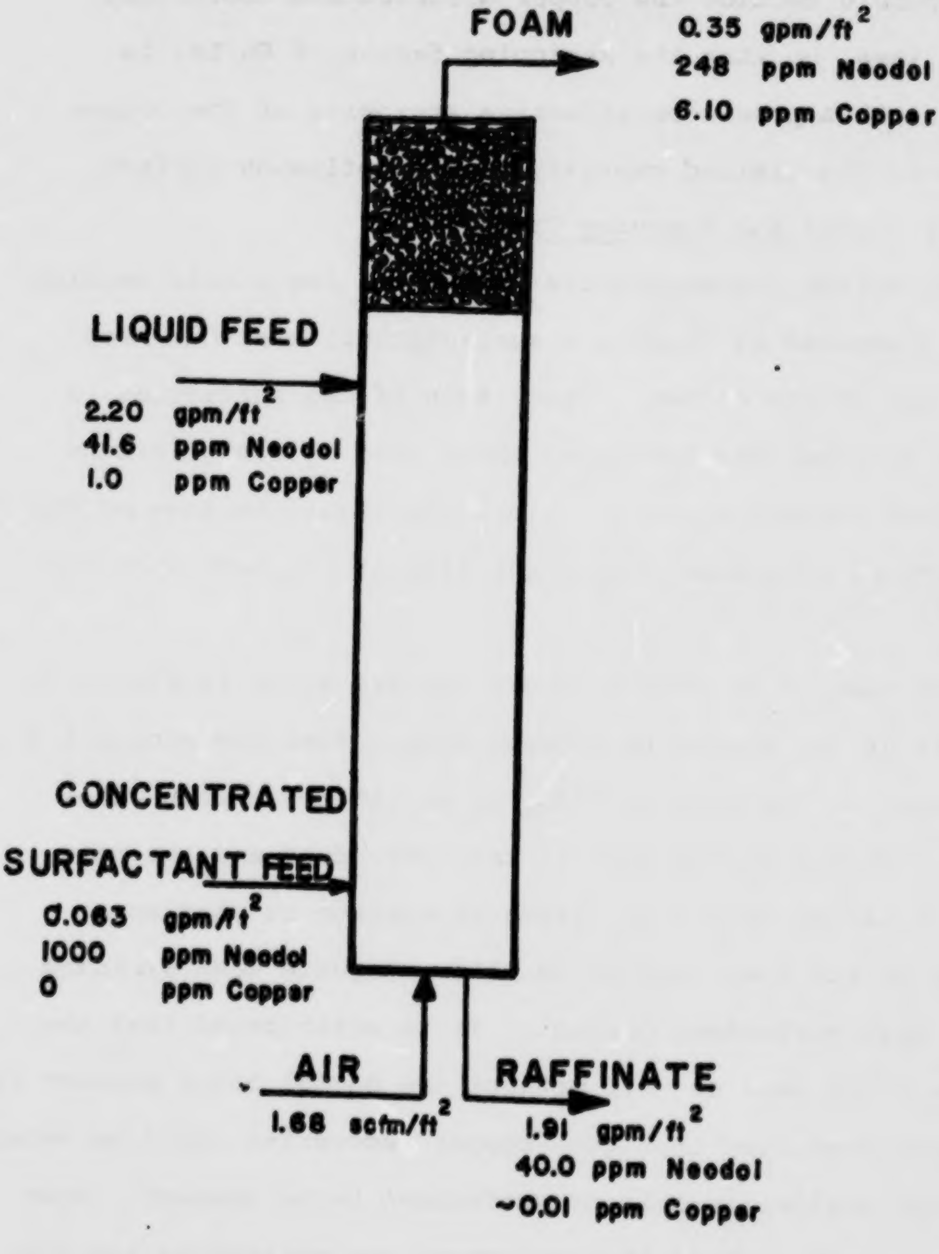
FOAM
0.35 gpm/ft^2
248 ppm Neodol
6.10 ppm Copper
LIQUID FEED
2.20 gpm/ft^2
41.6 ppm Neodol
1.0 ppm Copper
CONCENTRATED SURFACTANT FEED
0.063 gpm/ft^2
1000 ppm Neodol
0 ppm Copper
AIR
1.68 scfm/ft^2
RAFFINATE
1.91 gpm/ft^2
40.0 ppm Neodol
~0.01 ppm Copper

Fig. 9. Improved Copper Removal

foam section.

The effluent water from a process operating as shown in Figure 9 can be sent to a second foam (bubble) column for surfactant removal and recovery for recycle to the first column. Alternatively, this step can be carried in an added lower section of the main column. The feasibility of high surfactant removals on a large scale is shown and discussed elsewhere (Valdes-Krieg, et al, 1974).

Acknowledgement

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THE ADSORPTIVE BUBBLE SEPARATION TECHNIQUES

(The "Adsubble" Techniques)

Foam Fractionation and Allied Processes

by

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Traces of Heavy Metals in Water: Removal Processes and Monitoring

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Princeton University
Princeton, New Jersey

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INTRODUCTION

The adsorptive bubble separation techniques (which are often abbreviated as the adsubble techniques) are processes for partially separating the constituents of solutions or suspensions through the adsorption or attachment of these constituents at the surfaces of ascending bubbles (Lemlich, 1966a, 1973). These processes remove solute or particulates from the liquid, not vice versa as in, say, evaporation. Furthermore, the selectivity of removal is often quite high and remains undiminished as the removal proceeds. Therefore, some of these processes would seem to be worth considering as possible candidates for the economical removal of trace heavy metals from water. Accordingly, this paper presents an overview of various adsubble methods, with an emphasis on the author's own work. A compilation of recent publications that report the separation of heavy metals through the use of the adsubble methods is also presented. For further information regarding the adsubble methods, the reader is referred to a recent comprehensive book (Lemlich, 1972a).

MICROPARTICULATE FOAM PROCESSES

Foam fractionation is a technique for partially separating dissolved (or sometimes colloidal) material by adsorption at the surfaces of bubbles that ascend through the solution to form a foam which is then removed overhead (Karger, et al., 1967; Lemlich, 1968a/69, 1972b). If the material to be removed (termed the "colligend") is itself surface inactive, it may still be foamed off by adding a suitable surface active "collector" that will combine with it. This union may occur by counterionic attraction, formation of a complex, or otherwise. The colligend-collector product is termed the "sublate". If the colligend is ionic, the technique is sometimes called ion flotation (Sebba, 1962). However, when ion flotation gives rise to an insoluble sublate or scum, it belongs more properly in the next section under macroparticulate foam processes (Karger, et al., 1967, Pinfold, 1972a).

Foam fractionation is a partition process, at least for dissolved material. The separation attainable in the simple mode [equilibrium operation] is readily calculated from the solute surface excess which is approximately the concentration of material at the bubble surface (Brunner and Lemlich, 1963). The separation can be cascaded to give better results by employing a countercurrent mode such as stripping operation [which involves liquid entering the rising foam], enriching operation [which involves collapsed foam -- termed "foamate" - trickling down as reflux through the rising foam], or combined operation [which is stripping operation plus enriching operation] (Leonard and Lemlich, 1965a; Fanlo and Lemlich, 1965). These modes are illustrated in Figure 1. External reflux is made available by the return of externally mechanically collapsed foam (Lemlich and Lavi, 1961). Induced internal reflux results from instability within the rising column of foam (Lemlich, 1968b, 1972c).

For the countercurrent modes, theoretical stages or transfer units can be computed in terms of a downflowing stream of interstitial liquid and an upflowing stream of interstitial liquid plus bubble surface (Lemlich, 1968b). Foams of high liquid content are undesirable in that they permit excessive channeling and disruption of the countercurrent pattern of flow. HTU values of a few cm have been reported under good conditions (Hastings, 1967; Jashnani and Lemlich, 1973). The rate of foam overflow can be estimated from a theory for interstitial drainage through the matrix of randomly oriented veins [called Plateau borders] of noncircular cross section in a foam of low liquid content (Leonard and Lemlich, 1965a,b; Fanlo and Lemlich, 1965; Shih and Lemlich, 1967, 1971; Lemlich, 1968c, Jashnani and Lemlich, in press). This drainage is subject to both a liquid viscosity within the veins and a surface viscosity which is the resistance to shear at their surfaces. The effective surface viscosity of some common surfactants in water at room temperature is of the order of 10^{-4} dyne sec/cm.

MACROPARTICULATE FOAM PROCESSES

If, through the addition of a precipitating agent, the colligend is first made to precipitate, and then a collector is added so that the precipitate can be foamed off, the process is termed precipitate flotation of the first kind (Pinfold, 1972b) However, if there is no separate precipitating agent and the collector is surface inactive yet forms with the colligend a precipitate with a hydrophobic surface (so as to make the precipitate surface active and thus removable by bubbling), then the process is called precipitate flotation of the second kind (Pinfold, 1972b). Precipitate flotation generally requires less surfactant than does foam fractionation; no more than the surface of the precipitate need be coated in the first kind, and no surfactant at all is required in the second kind. But of course a precipitating agent is required. Adsorbing colloid flotation is the "piggy back" process whereby a solute is adsorbed on a colloid which is then foamed off (Karger, et al., 1967), perhaps with the aid of a collector.

All of the foregoing should be distinguished from the process of ore flotation which is used in the mineral industries to separate one kind of already solid macroparticle from another via selective wetting and bubbling (Gaudin, 1957; Fuerstenau and Healy, 1972). Flotation is also employed to collect macroparticles on a less selective basis, as in sewage treatment(Jenkins, et al., 1972).

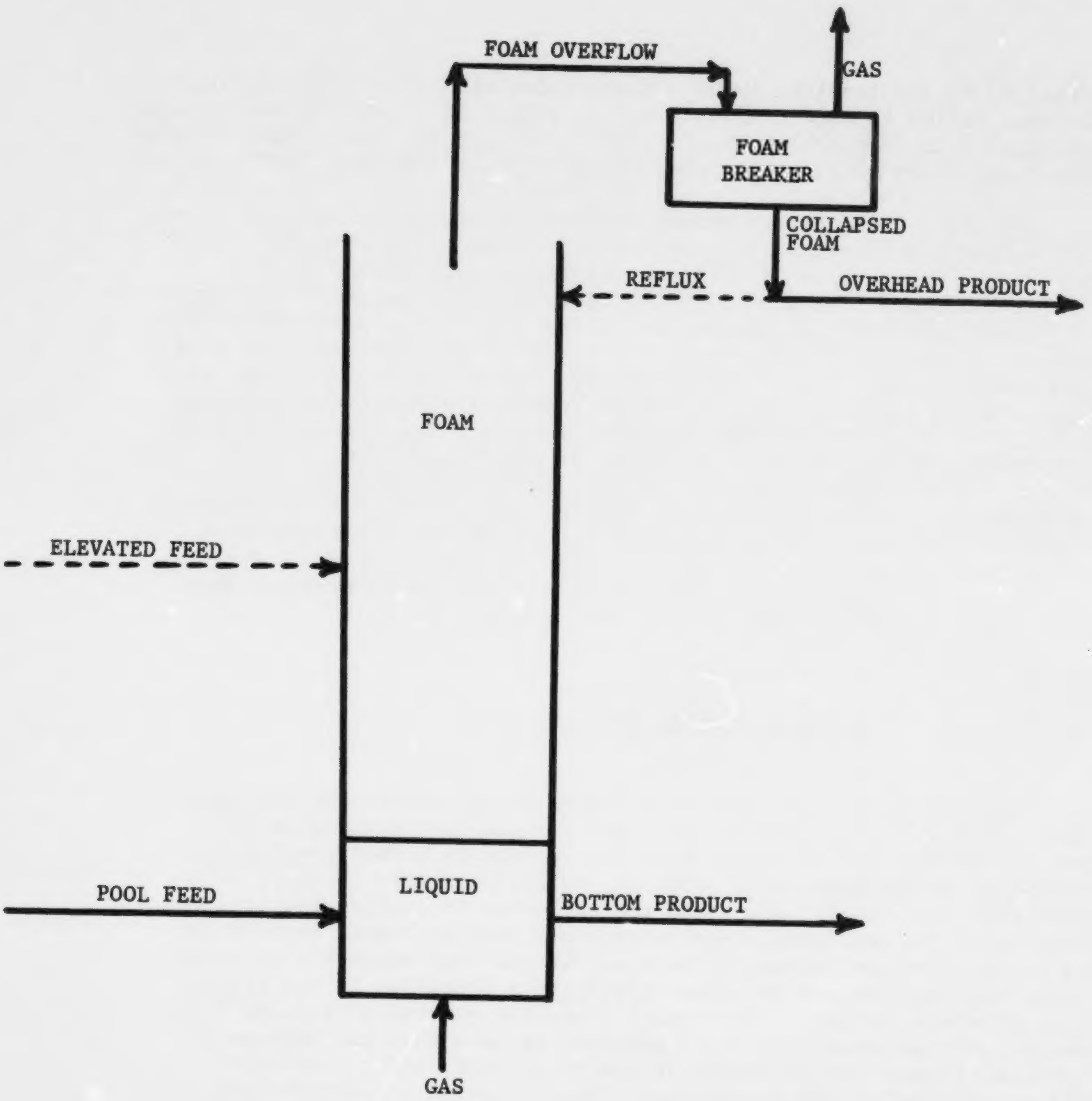
FOAM OVERFLOW
GAS
FOAM BREAKER
COLLAPSED FOAM
REFLUX
OVERHEAD PRODUCT
FOAM
ELEVATED FEED
POOL FEED
LIQUID
BOTTOM PRODUCT
GAS

Figure 1. Continuous foam fractionation: The solid lines show operation in the simple mode. For the stripping mode, the pool feed is replaced by an elevated feed [shown dashed] into the foam. For the enriching mode some collapsed foam is returned as reflux [shown dashed] to re-enter near the top of the column. For the combined mode, both stripping and enriching are employed.

FOAMLESS PROCESSES

Even if no foam forms, bubbling may still produce a concentration gradient within an elongated vertical pool by virtue of the carryup of surface active material on the bubble surfaces (Dorman and Lemlich, 1965, Lemlich, 1972d). The gradient represents a partial separation: stripping at the bottom of the pool where adsorption first takes place, and enriching at the top where the escaping bubbles deposit their carryup. The process is termed bubble fractionation (Lemlich, 1964). It can be employed by itself, or it can be used in conjunction with foam fractionation as illustrated in Figure 2. Bubble fractionation can raise a concentration up to the foaming threshold.

Bubble fractionation can be analyzed in a simplified manner in terms of the adsorbed carryup which promotes the concentration gradient, and the dispersion in the liquid which diminishes the gradient (Lemlich, 1966b/67). A more detailed analysis takes into consideration the variation in the rate of adsorption around the leading surface of the bubble and the behavior of the turbulently discharging wake (Cannon and Lemlich, 1972). Either approach shows that the degree of separation increases as the pool is vertically elongated, and (unfortunately) decreases as the pool is widened (Harper and Lemlich, 1966; Shah and Lemlich, 1970).

If a layer of some immiscible liquid is placed on top of the main liquid to trap the adsorbed carryup, the process is called solvent sublation (Sebba, 1962; Karger , 1972). In general, the degree of entrapment exceeds the equilibrium solubility in the upper liquid.

There is theoretically no lower concentration limit for the operability of either solvent sublation or bubble fractionation.

CAUTION AND COMMENT

The bursting bubbles from any adsubble process may throw off an aerosol of extremely fine droplets that can carry appreciable quantities of adsorbed material. With certain systems, this material can be noxious, toxic, or even pathogenic. So, to avoid converting a problem in water pollution into a problem in air pollution, it may be necessary to remove these airborne particles by some suitable means. However, a simpler approach might be just to recycle the air (or other gas) back to the blower for rebubbling through the liquid pool.

Recycling the gas would also allow one to incorporate a suitable organic vapor into the gas stream without loosing any of this vapor, except by slight solution in the liquid or through other minor losses.

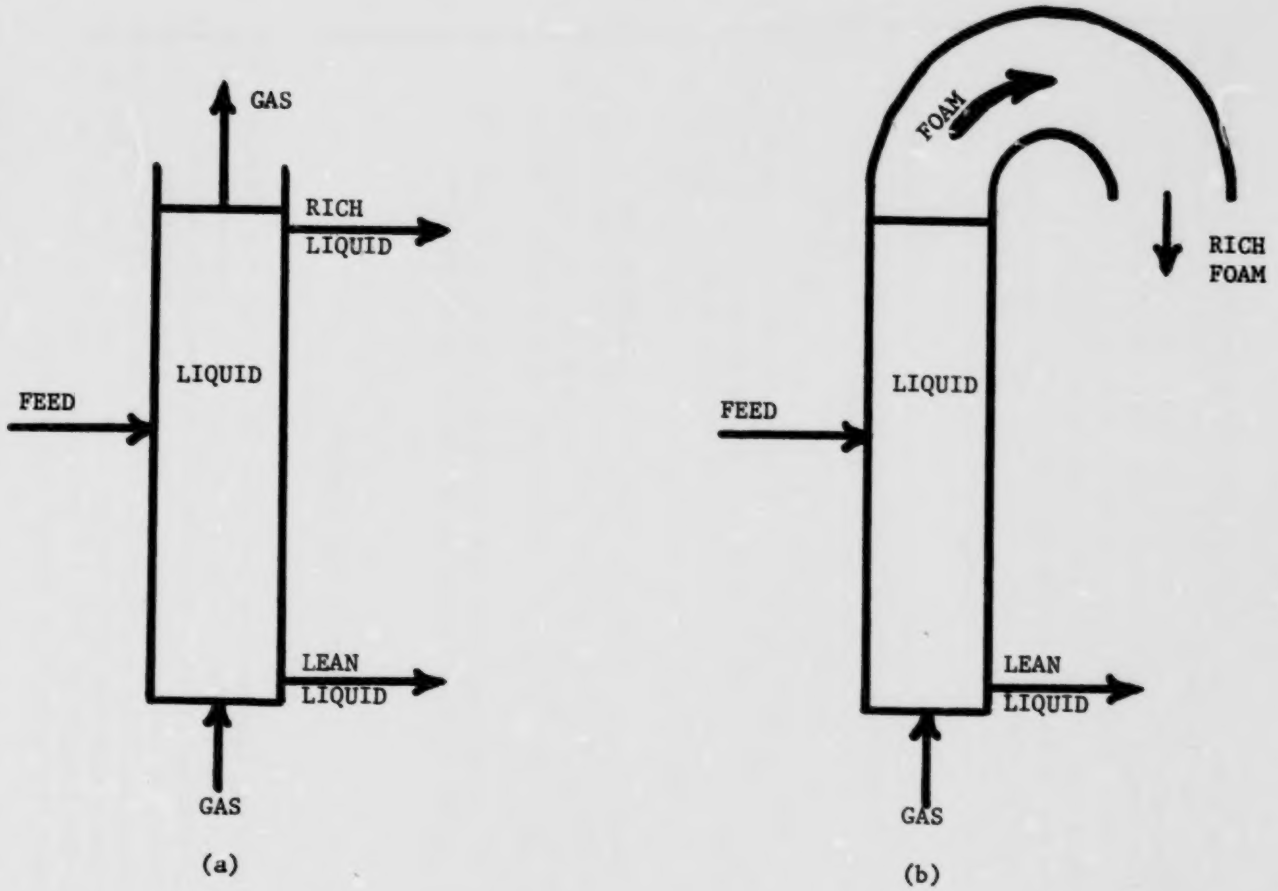
GAS
RICH
LIQUID
FEED
LIQUID
LEAN
LIQUID
GAS
(a)
FOAM
RICH
FOAM
FEED
LIQUID
LEAN
LIQUID
GAS
(b)

Figure 2. Continuous bubble fractionation: (a) alone; (b) in conjunction with foam fractionation.

The presence of certain such vapors reportedly increases the selectivity of adsorption from the liquid (Maas, 1969, 1970).

It is interesting to note that the production of very fine airborne droplets with material preferentially adsorbed at their surfaces seems to occur on a large scale at the surface of the sea in the process of forming the marine aerosol. The phenomenon itself, as well as its effect on the atmosphere and elsewhere, is a subject of continuing study by a number of investigators. The interested reader might consult the proceedings of a recent conference on sea-air chemistry which are published in volume 77, issue 27, of the J. Geophs. Res. (Oceans and Atomospheres), 1972. [A contribution of a general nature by the present author is also included (Lemlich, 1972f)]. Other related papers appear in later issues of the said journal.

SYSTEMS SEPARATED

A wide variety of substances, including ions of heavy metals, have been separated by means of the adsubble techniques. For a compilation of recently reported separations, the reader is referred to Lemlich (1972e). Earlier separations are compiled in Lemlich (1968d, 1972a), and in Karger and DeVivo (1968). Still earlier work is listed in Rubin and Gaden (1962).

The remainder of the present paper covers reports of heavy-metal separations that have chiefly appeared quite recently. These are not included in any of the aforementioned compilations.

These recent reports are listed below in alphabetical order by the chemical symbols of the heavy metals involved, with some miscellany at the end. As a further guide to the reader, the citations include the complete titles and, in certain cases, some additional information in brackets.

Ag - Charewicz and Walkowiak (1972), Grieves and Bhattacharyya (1972).

Au - Charewicz (1973a), Charewicz and Niemiec (1969b), Charewicz and Walkowiak (1972).

Cd - Huang (1973?), Shimoiizaka, et al. (1970, 1972a), Takahashi, et al. (1971).

Ce - Kepak and Kriva (1972), Pustovalov and Pushkarev (1972), Robertson and Vermeulen (1969).

Co - Charewicz and Walkowiak (1972), Jurkiewicz and Waksmundzki (1973), Waksmundzki and Jurkiewicz (1973).

Cr - Grieves and Bhattacharyya (1972), Grieves, et al. (1973).

Cu - Huang (1973?), Kim and Zeitlin (1972), Pearson and Shirley (1973), Takahashi, et al. (1972).

Fe - Horizons (1971), Shimoiizaka, et al. (1972b).

Hg - Nanjo, et al. (1971, 1972).

Mn - Horizons (1971).

Mo - Charewicz (1973a,b), Charewicz and Walkowiak (1972).

Nd - Robertson and Vermeulen (1969).

Ni - Charewicz and Walkowiak (1972), Jurkiewicz and Waksmundski (1973), Pearson and Shirley (1973), Waksmundski and Jurkiewicz (1973), Zhidrova, et al. (1972).

Pb - Huang (1973?)

Pd - Charewicz and Walkowiak (1972), Walkowiak and Bartecki (1973a).

Pm - Kepak and Kriva (1972).

Pt - Charewicz and Walkowiak (1972), Walkowiak and Bartecki (1973b).

Re - Charewicz (1973a,b), Charewicz and Niemiec(1969a), Charewicz and Walkowiak (1972).

Ru - Kepak and Kriva (1970).

Sm - Robertson and Vermeulen (1969).

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REMOVAL OF HEAVY METALS BY CONVENTIONAL TREATMENT

by Gary S. Logsdon and James M. Symons, respectively, Research Sanitary Engineer and Chief, Standards Attainment Branch, Water Supply Research Laboratory, National Environmental Research Center, U.S. Environmental Protection Agency (EPA) Cincinnati, Ohio.

INTRODUCTION

As a regulatory agency, the U. S. Environmental Protection Agency (EPA) sets Drinking Water Standards for a number of substances in water, including certain inorganic constituents (1). Another function of the Agency is to determine the efficacy of present water treatment technology to meet these Standards. Knowing whether methods now used by the water utility industry can remove environmental levels of inorganic contaminants is necessary and for substances not removed or reduced to the limit of the Standards, new technology needs to be developed.

For these reasons, a program of research on the removal of trace inorganic substances by water treatment processes has been underway for over 2 years at the Water Supply Research Laboratory of EPA's National Environmental Research Center in Cincinnati. Constituents in the proposed EPA Drinking Water Standards that have been or are being studied are mercury, barium, arsenic, and selenium. Among those considered for possible future study are lead, cadmium, and chromium.

This paper summarizes the results obtained thus far: information on removing methyl mercury, inorganic mercury, barium, selenate, selenite, arsenite, and arsenate. Treatment processes studied in the laboratory are iron coagulation, aluminum coagulation, lime softening, excess lime softening, and activated carbon adsorption. Although no single treatment process has been found effective for every contaminant studied, recommendations based upon the laboratory results are made for the treatment processes likely to be most effective for removing each of the contaminants.

REVIEW OF LITERATURE

A number of studies of trace element removal have been conducted. Barnett et al. reported that barium concentration of 20 to 50 μg/l were reduced very little or not at all by alum coagulation at Denver's water plants (2). None of the other elements studied at Denver has yet been investigated in the program of studies reported herein.

Decontamination of radioactive waters was studied at Oak Ridge in the early 1950's (3). In that work, removals of a mixture of ^{140}Ba and ^{140}La by coagulation ranged from 1 to 84 percent and averaged from 44 to 59 percent. Chemical doses (ferric sulfate, ferric chloride, or alum) ranged from 17 to 102 mg/l. Activated silica and lime or soda ash were also added. Ninety percent removals could be obtained by lime softening. Ion exchange experiments with greensand showed 96.3 percent removal of the barium-lanthanum mixture.

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Actual chemical concentrations were not stated. Barium-140 has a specific activity of 7.3×10^4 Ci/g, so it would be detectable in microgram or nanogram per liter concentrations. Thus, there could have been much less than 1 mg/l of barium in the water tested at Oak Ridge.

Cherkinskii et al. reported results of pilot plant studies of alum coagulation, sedimentation, and filtration for removal of chemical substances (4). Arsenic originally present at concentrations of 0.5 to 1.0 mg/l was removed 50 to 60 percent. For concentrations of 2 to 10 mg/l of selenium, removals ranged from 50 to 70 percent. The final concentrations reported in this work, however, exceeded the proposed USEPA Drinking Water Standard of 0.1 mg/l for arsenic and 0.01 mg/l for selenium.

Removal of arsenic by coagulation was studied by Gulledge and O'Connor at the University of Illinois (5). When the initial arsenate concentration was 0.05 mg/l, removals in excess of 90 percent could be attained, depending on coagulant dose and pH. Coagulation with ferric sulfate was more effective than coagulation with alum at concentrations of up to 50 mg/l for either coagulant. Also at Illinois, Ebersole (6) found that mercuric chloride at 5.8 μg/l or 50 μg/l could be removed from water by alum or iron coagulation (5). Removals generally ranged from 30 to 70 percent. Ferric sulfate was more effective than was alum when both were added at a nominal dose of 20 mg/l.

Laboratory and field studies on arsenic removal from drinking water in Taiwan were described by Shen (7). The arsenic content of some well waters there was reported to be in the range of 0.6 to 2.0 mg/l. High arsenic concentrations in drinking water had been associated with the occurrence of black-foot disease, so Shen conducted a long and thorough investigation of arsenic removal by coagulation.

Although arsenic could be removed by coagulation, treatment of the groundwater with an oxidant was necessary to obtain a residual arsenic concentration of 0.05 mg/l or less. For example, with 1 mg/l of arsenic in the raw water, coagulation with 50 mg/l of ferric chloride gave 90 percent removal. Coagulation with the same dose of ferric chloride after oxidation with 20 mg/l of chlorine resulted in 98.7 percent arsenic removal. In this case, the initial arsenic content was 0.8 mg/l; the residual arsenic was 0.01 mg/l; the chlorine residual was 1.0 mg/l. This example indicates that the oxidation state of the arsenic may have an important bearing on its removal by various unit processes.

Angino et al. (8) reported an arsenic removal of 87 percent (with the reduction of a 3.1 mg/l initial arsenic concentration to 0.4 μg/l) at the Lawrence, Kansas, water plant, which uses the cold lime softening process. In laboratory work, they obtained 85 percent removal with cold lime softening when the original arsenic content was 0.2 mg/l.

Linstedt et al. (9) studied removal of cadmium, chrome, silver, and selenium in advanced waste treatment processes. A small pilot plant was employed to treat 105 gallon (398 l) batches of secondary sewage effluent. They reported that lime coagulation to pH 11 removed only 16.2 percent of the selenium added as selenite. The initial selenium concentration was $\leq$ 12.8 μg/l in this study. On the other hand, about 35 percent of the selenite was removed by activated carbon, and this was attributed to interaction with organic matter, followed by carbon adsorption of the organics. Finally, removal by cation and anion exchange exceeded 99 percent.

EXPERIMENTAL METHODS

Experiments described in this report were performed in the laboratory on a jar-test apparatus. The methods used have been described by Logsdon and Symons (10). Waters used in the work were raw Ohio River water;raw well water from Glendale, Ohio; Cincinnati tap water; and a Midwestern groundwater containing barium. Except for the barium-laden water, waters were dosed with the contaminant to be studied, given 2 minutes of rapid mix after addition of the treatment chemical and 20 minutes of slow mix for coagulation tests, or they were given 3 minutes of rapid mix and 30 minutes of slow mix for softening. One hour of settling was used for all tests. Settled jar-test samples from barium, arsenic, and selenium experiments were centrifuged to attain the final clarification normally accomplished by filtration in a water works. In tests of mercury removal by coagulation, clarification was very good (most samples below 1.0 turbidity unit (T.U.) and all below 5 T.U.) and samples were not centrifuged. Clarification by centrifuge was used in softeni tests involving mercury and in all powdered activated carbon adsorption tests. Analyses were made for pH, turbidity, alkalinity, and in some cases, hardness, as well as for contaminant concentration.

Two methods were used for metals analysis. An atomic absorption spectrophotometer was used for analysis of nonradioactive contaminants in significant portions of the mercury, barium, and arsenic work, and occasionall in the selenium experiments. Methods have been described by Kopp et al. (11), McFarren (12), and Caldwell et al. (13). In some experiments, radiotracers were used along with stable carriers. The tracers were ^{203}Hg as methyl mercur and as mercuric nitrate, ^{74}As as arsenate, ^{76}As as arsenite, ^{75}Se as selenite and selenate, and ^{133}Ba as barium chloride. Radioactivity was measured using a shielded NaI (Tl) crystal and a single channel analyzer. Samples having a volume of 100 ml were counted in 1-quart, plastic-lined, disposable paper containers. When radiotracers were used, the initial contaminant concentratio was determined by adding the radioisotope, plus a known volume of stock carrie solution, to the water being treated and calculating the initial metal concentration. Removal percentage was the percentage of reduction of radioactivity.

To check the analytical work and to verify the removal of contaminants by coagulation of softening, material balances were performed. These, although desirable, were done only occasionally for experiments not employing radiotracers, because of the large amount of extra work involved. Because analysis was so simple, however, balances were done in almost all radiotracer tests. A balance involved calculation of the amount of contaminant or radioactivity in the untreated water vs. the sum of contaminant or radioactivity in settled water and in the recovered sludge.

Material balance results were considered acceptable for atomic absorption data and very good for tracer experiments. In the latter, tracers balanced to within ± 3 percent in 63 percent of the tests and to within ± 5 percent in 80 percent. Twenty-two of 365 experiments had divergences in excess of 10 percent. Results of the material balances confirmed the quality of the analyses and demonstrated the fate of contaminants in the treatment processes.

RESULTS AND DISCUSSION

Mercury

The results of mercury removal studies of the Water Supply Research Laboratory, presented in more detail elsewhere by Logsdon and Symons (10), are summarized here. In coagulation experiments involving Ohio River water, initial mercury concentration did not appear to be related to removal of either methyl mercury or inorganic mercury in the 2 to 16 μg/l concentration range. Raw water turbidity was considerably more important, as can be seen in Figures 1 and 2. Because mercury also could be removed by removal of turbidity in the absence of coagulants, adsorption on natural turbidity was thought to be an important factor in mercury removal by coagulation. When coagulant doses were selected to give good clarification in the treatment process, ferric sulfate was more effective than alum -- often giving 50 percent removal of inorganic mercury. Methyl mercury removals were low for ferric sulfate or alum, usually 30 percent or less.

Mercury removal by lime softening was tested using Glendale, Ohio, well water, with about 300 mg/l hardness as calcium carbonate. Figure 3, which also shows the relationship of pH and hardness, shows that softening the water to pH 9.5 removed 30 to 40 percent of the inorganic mercury. This could be increased to 50 percent by coagulating the softened water with ferric sulfate, a step that might be done to remove the pinpoint calcium carbonate that failed to settle. Excess lime softening to pH 10.6 to 11 resulted in formation of a voluminous magnesium hydroxide floc, good clarification, and 70 percent removal of inorganic mercury. Removal of methyl mercury by softening could not be detected at either pH range.

Preliminary experiments with mercury removal by ion exchange have been carried out. As much as 98 percent of the mercury added to distilled water as $CH_3{}^{203}HgCl$ and $^{203}Hg(NO_3)_2$ and buffered to desired pH ranges could be removed by decontamination columns containing IR 120 and IRA 458 (Rhom and Haas)* ion exchange resins. These columns are normally used to remove excessive radioactivity from solutions at the conclusion of experiments.

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*Mention of commercial products does not imply endorsement by the U.S. Environmental Protection Agency.

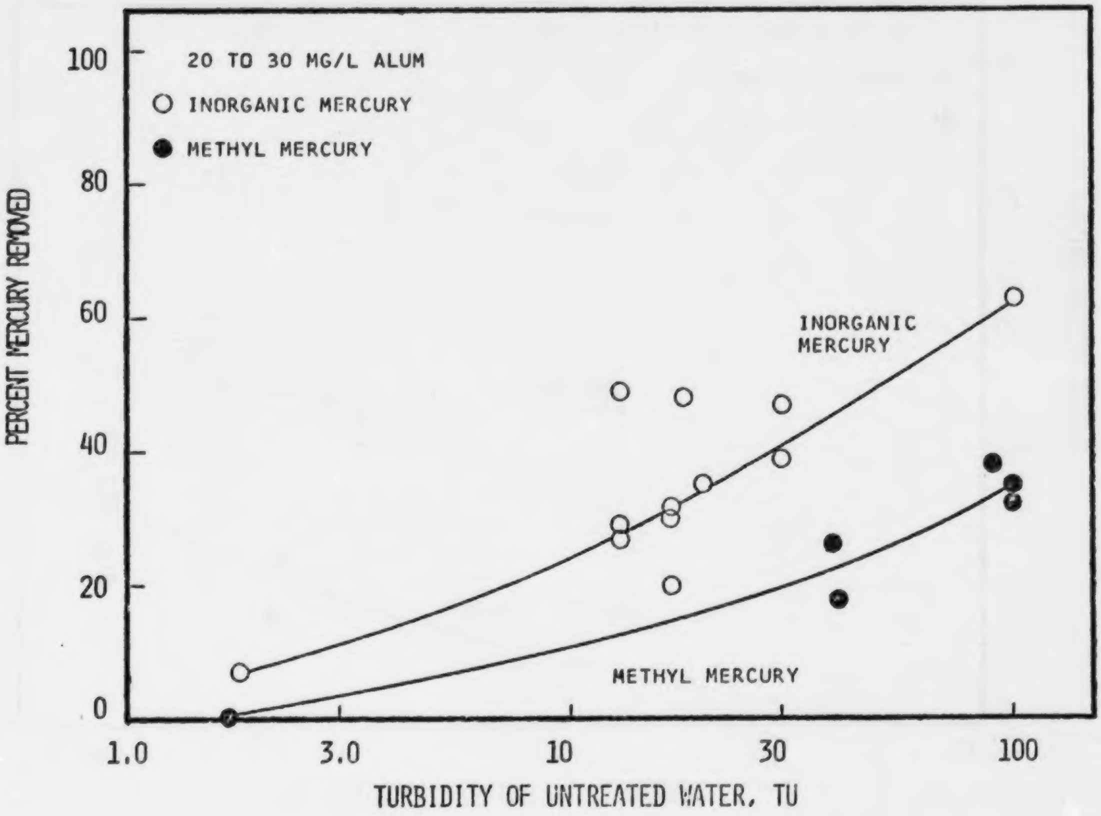

Figure 1. Turbidity vs. Mercury Removal by Alum Coagulation.

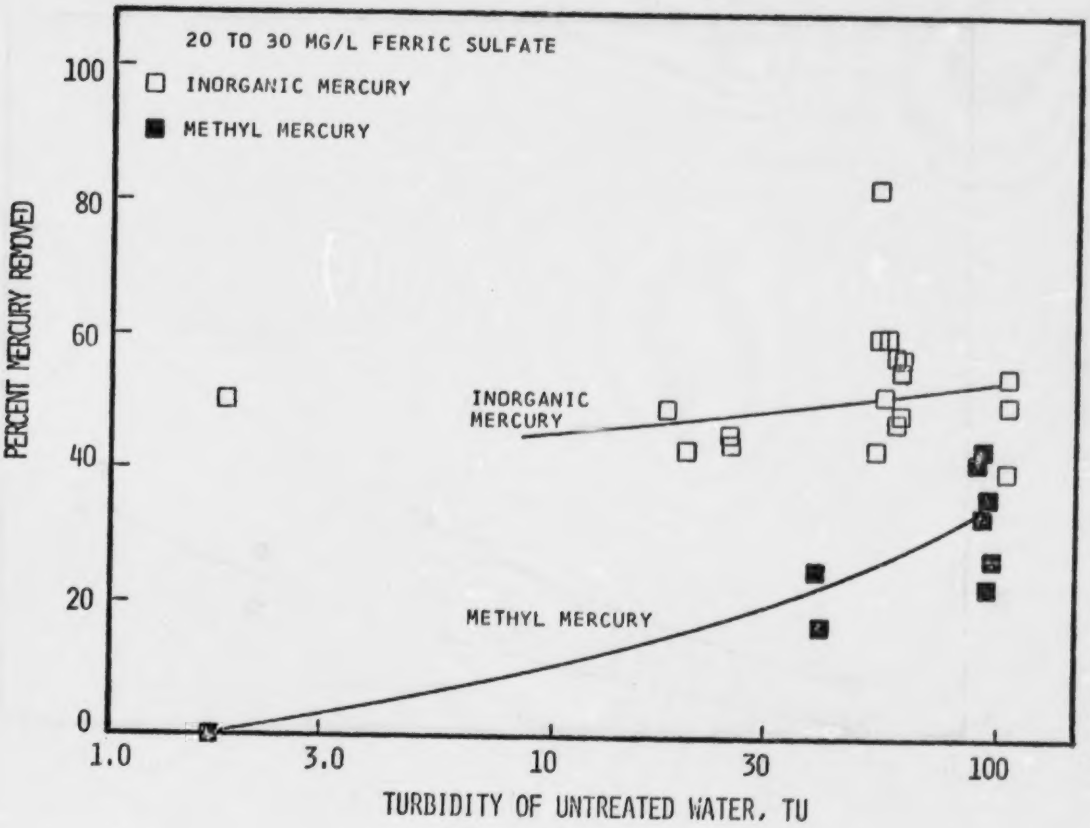

Figure 2. Turbidity vs. Mercury Removal by Iron Coagulation.

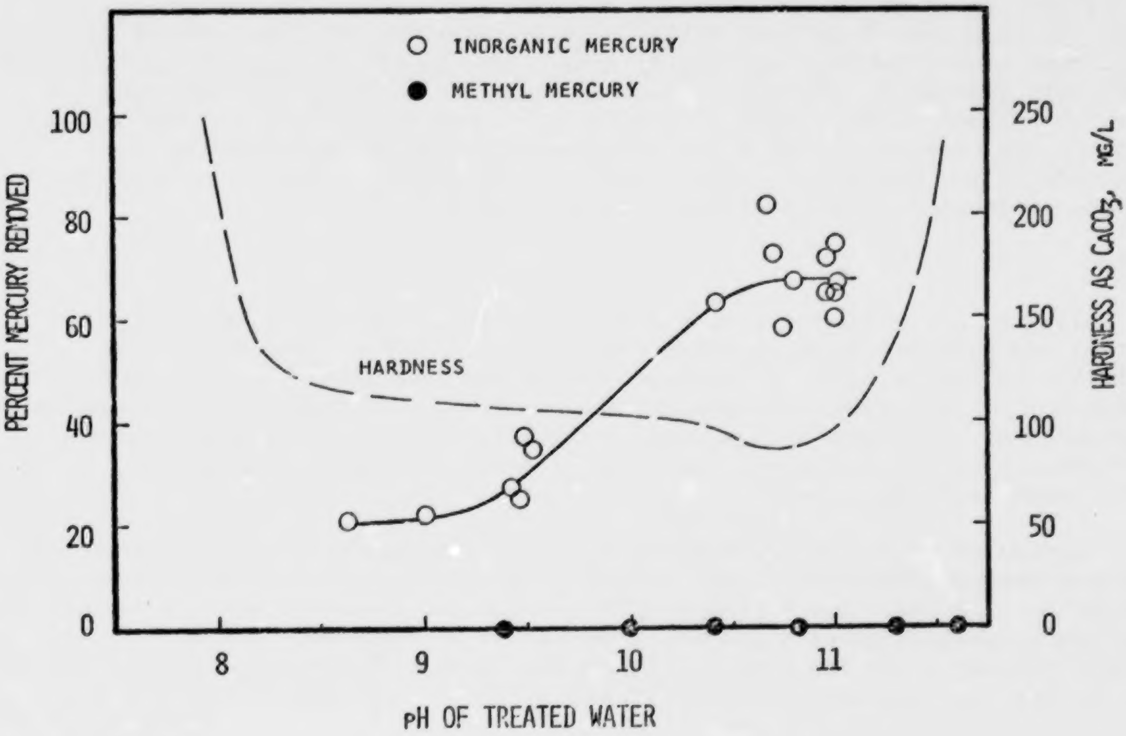

Figure 3. Mercury Removal by Lime Softening.

In another exploratory group of tests, the use of Activex (J.M. Huber Corp.) heavy metal ion exchanger (a synthetic silica material) to remove mercury was studied. This powdered-type material is added in much the same way as powdered activated carbon. Preliminary results indicate inorganic mercury can be removed, but efficiency for methyl mercury removal is poor. Inorganic mercury was reduced from 10 to 5 μg/l (50 percent) by 80 mg/l of treatment chemical. Further investigations are needed before firm statements can be made on this process.

Mercury removal by activated carbon was evaluated using granular carbon in columns and powdered carbon in jar tests. Both methyl mercury and inorganic mercury were adsorbed on the carbon. This process has been discussed by Sigworth and Smith (14). In an experiment to learn how activated carbon might improve mercury removal in a plant treating surface water, powdered activated carbon was added to Ohio River water in various doses. The water was stirred for 10 minutes and then 30 mg/l alum was added. The results (Figure 4) show that 40 percent of the inorganic mercury could be removed by coagulation alone, and that increasing amounts of removal occurred as the activated carbon dose increased. Because the activated carbon doses applied are much larger than those normally used in water plants, the doses typically applied for taste and odor control would not be very effective for mercury removal. Nevertheless, for control of mercury during times of known pollution incidents, high-dose activated carbon treatment should be effective.

Barium

Barium is not often found in waters in excess of the 1 mg/l limit of the existing and proposed Drinking Water Standards, possibly because of the low solubility of barium sulfate. However, barium has been detected in certain groundwaters in the Midwest in concentrations of up to 10 mg/l (15,16). Samples of groundwater containing barium were obtained from Illinois, so that treatment experiments could be conducted. The sulfate concentrations in raw water samples were less than 1 mg/l.

Coagulation with aluminum sulfate and also with ferric sulfate was expected to remove barium effectively. The sulfate added in the treatment process was expected to form insoluble barium sulfate because the treatment process would cause the solubility product for this compound to be exceeded. The anticipated results were not achieved, however (Figure 5); removal did not exceed 30 percent when the initial barium content was in the 7 to 8 mg/l range.

A possible reason for poor barium removal was supersaturation of barium sulfate. If a nonequilibrium condition existed, perhaps, with the passage of time, the distribution of dissolved and precipitated barium would tend toward equilibrium. A series of experiments was set up in which water was treated with either 100 mg/l of ferric sulfate or 100 mg/l of alum. Settled waters were withdrawn and kept in test jars. At time intervals of 3, 6, 12, and 24 hours after the first treatment, a second stage of coagulation was carried out. In the second treatment, the coagulant dose was 20 mg/l of the same chemical used for the first stage of the treatment.

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*Mention of commercial products does not imply endorsement by the U.S. Environmental Protection Agency.

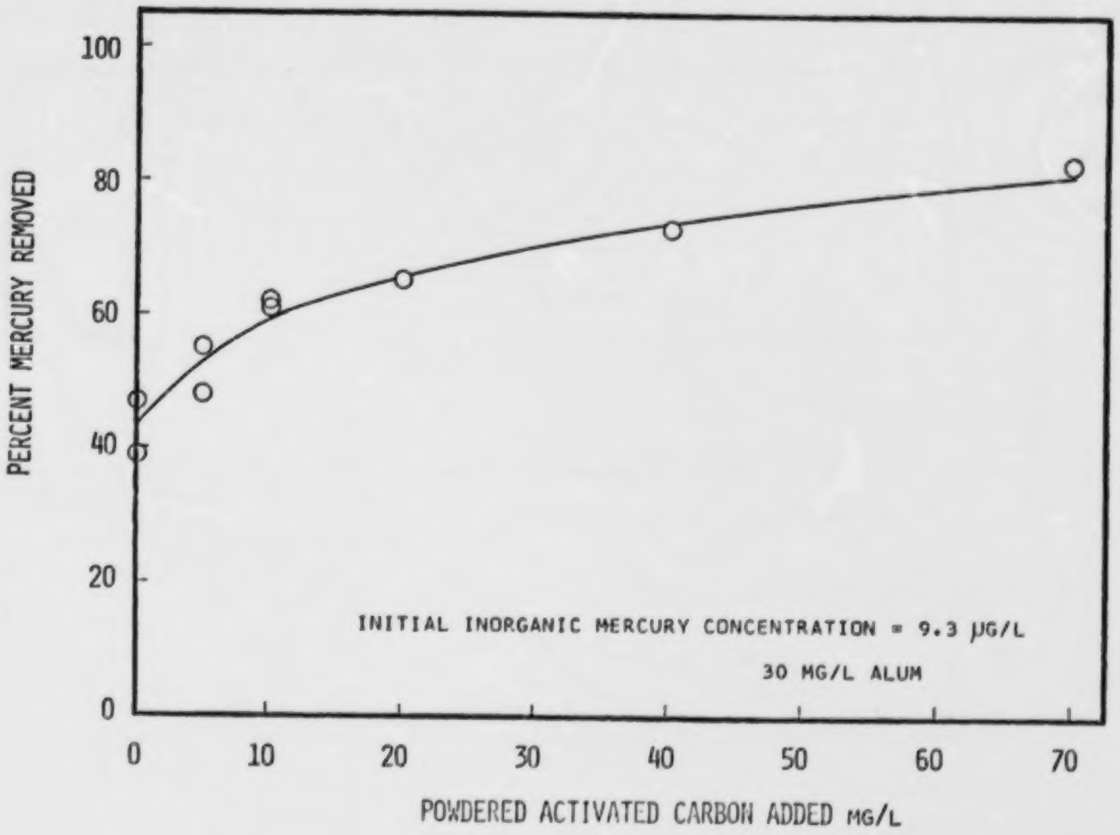


Figure 4. Inorganic Mercury Removal by Powdered Activated Carbon and Alum Coagulation.

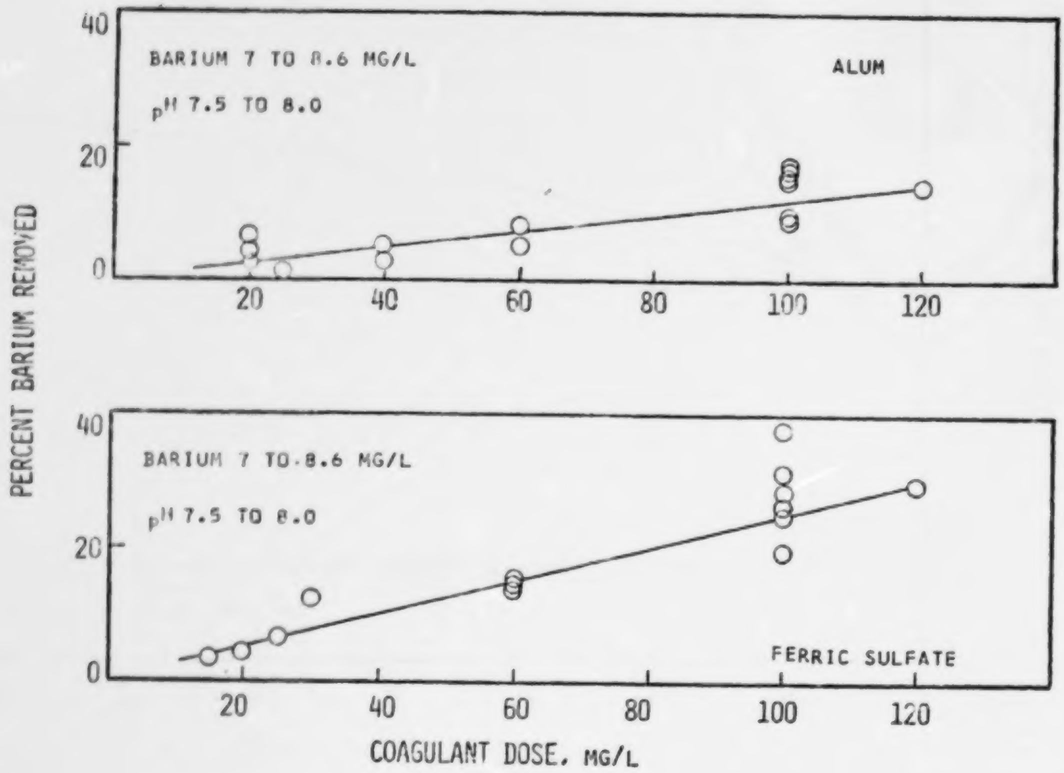


Figure 5. Barium Removal by Coagulation.

The results of barium removal by two-stage coagulation (Figure 6) give strong support for the suggestion that barium sulfate was supersaturated after the first coagulation. Better barium removals occurred when greater time was allowed for the supersaturated barium sulfate to form solid crystals that could be removed by the second coagulation step. This result does not give much encouragement to the design engineer, however, because two-step coagulation would be most costly than treatment in a single stage and providing sufficient volume to store 24 hours of accumulated treated water between the two treatment steps would add further capital expense.

Barium removal by lime softening was also studied, using water containing 7 to 8 mg/l of barium. As the pH of the treated water increased above 9, barium removal increased (Figure 7) and barium removals exceeded 90 percent in the range from pH 10 to pH 11. Maximum removal was nearly 98 percent.

Precipitation of barium carbonate is the mechanism suggested for barium removal by softening. On the basis of the raw water barium concentration and the alkalinity, adding lime to convert bicarbonates to carbonates could cause the solubility product for barium carbonate to be exceeded. The tendency for lime softening to cause the barium carbonate solubility product to be exceeded would be greater as the lime dose increased, and this would be reflected with increasing barium removals as pH increased to the 10 to 11 range. Further increases of pH, >11, resulted in a sharp decline in barium removal. This may have been because barium carbonate was converted to the more soluble barium hydroxide.

On the basis of laboratory results, the most effective conventional water treatment process should be lime softening in a pH range of 10 to 11. This process in the laboratory gave removals as high as 98 percent. It should provide satisfactory treatment for waters containing up to 10 mg/l of barium.

A limited amount of other data is available. Samples of groundwater obtained before and after treatment in a full-scale ion exchange softening plant showed barium reduction from 11.7 to 0.18 mg/l, a 98 percent removal. The sodium concentration of the softened water was 125 mg/l. Because excess sodium, as well as excess barium, can be a health hazard (17), some persons whose doctors have prescribed a low-sodium diet find it necessary to drink bottled water rather than sodium-cycle ion-exchange-softened water. Sodium-cycle ion exchange for barium removal must be evaluated in this context. The high reduction by ion exchange also agrees with Oak Ridge data.

Further results of laboratory jar tests with the Activex resin and stable barium plus ^{133}Ba indicate that removals of 80 percent or more can be obtained when initial barium concentrations are in the 3 to 10 mg/l range and the Activex dose is about 400 mg/l. Both the ion exchange and heavy metal resin techniques merit further study. Finally, barium added as stable carrier and radiotracer was not removed in jar tests with powdered activated carbon. Thus, the most effective methods for control of barium would be ion exchange and lime softening; then coagulation; with activated carbon, the least effective.

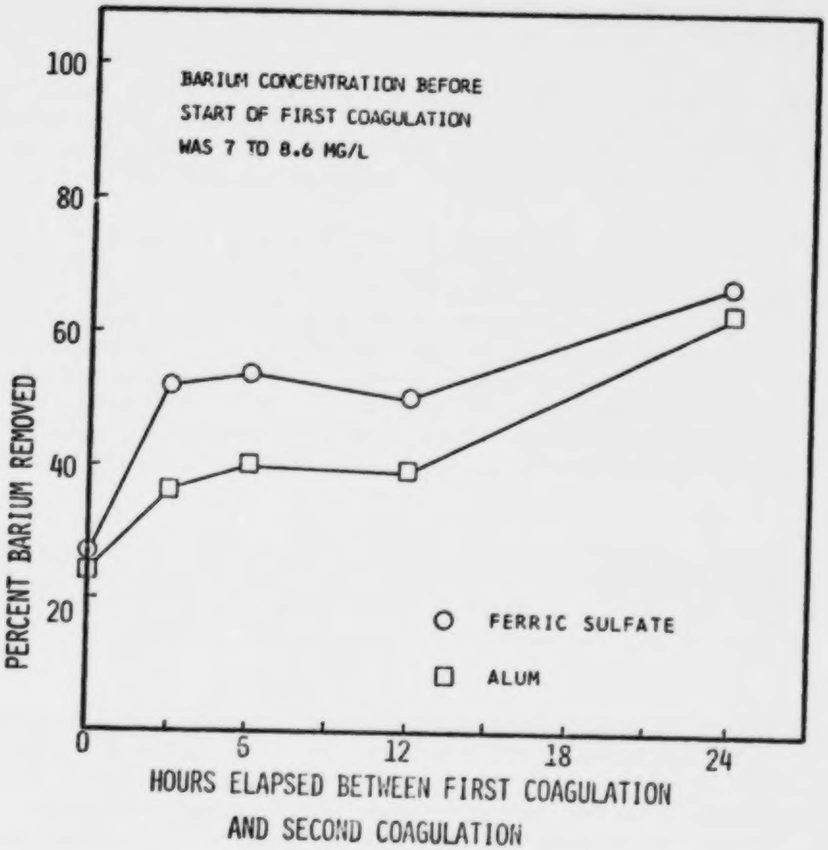


Figure 6. Effect of Time Interval on Barium Removal by Two-Stage Coagulation.

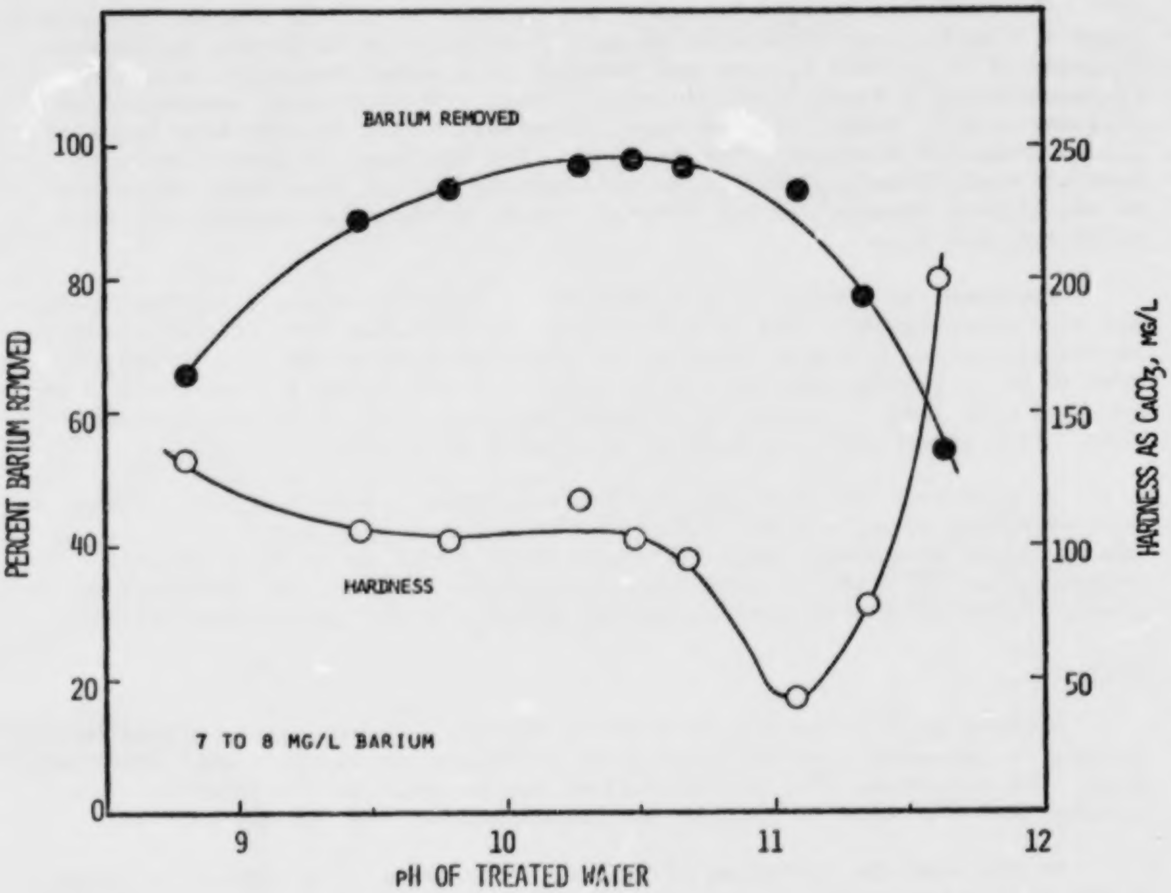


Figure 7. Barium Removal by Lime Softening.

Arsenic^{V}

Because Gulledge and O'Connor (4) thoroughly investigated the effect of pH, the emphasis in this present research was on the effect of coagulant dose on the removal of various concentrations of arsenic from surface waters (Ohio River water). Results are shown in Figure 8 for coagulation experiments in the pH range of 6.4 to 7.5. Initial arsenic^{V} concentrations varied from 0.10 to 20 mg/1.

The preferred type of treatment was related to initial arsenic concentrations. Below 1.0 mg/1, coagulation with 30 mg/1 of either alum or ferric sulfate gave removals of 90 percent or more and resulted in a water than would meet the proposed Drinking Water Standards of 0.10 mg/1. When arsenic^{V} concentrations exceeded 1 mg/1, ferric sulfate began to perform better than alum in terms of actual pounds of treatment chemical used. For instance, at 2 mg/1 arsenic^{V} removals with 30 mg/1 of ferric sulfate and 100 mg/1 of alum were comparable. At the highest arsenic^{V} levels studied, ferric sulfate was considerably more effective than alum.

Treatment of Glendale, Ohio, well water to which arsenate had been added was also investigated. The results (Figure 9) show that when initial arsenic concentration was 0.4 mg/1, removals by lime softening to pH 9 to 10 ranged from 40 to 70 percent and increased with pH. Better arsenic^{V} reductions were obtained when lime softening was followed by iron coagulation as a secondary step. This agrees with the findings of Angino et al. (8).

In work done for this report, arsenic^{V} removals were best with excess lime softening at pH 10.6 to 11.4. Data in Figure 8 indicate that 95 percent removal could be accomplished with excess lime softening up to an arsenic concentration of 12 mg/1. These results strongly suggest that municipal water plants should be able to control arsenic present in the pentavalent state.

Arsenic^{III}

Studies on the behavior of arsenite (arsenic^{III}) were also carried out. Arsenic in groundwater would probably be trivalent, so Glendale well water was used. The tracer was ^{76}As in the form of sodium arsenite. Radioactive decay calculations were made to correct for the effects of the 1.1 day half-life.

To minimize the oxidation of arsenic^{III} to arsenic^{V} by dissolved oxygen in the test water, nitrogen gas was bubbled through the test waters to purge the dissolved oxygen. Dissolved oxygen concentrations of the test water were generally below 0.5 mg/1 when the arsenic^{III} was added. Dissolved oxygen concentrations at the end of experiments were typically about 3 mg/1 when this analysis was performed. Under such conditions, oxidation of arsenic^{III} to arsenic^{V} should not have occurred to a significant extent except perhaps at the high pH values associated with excess lime softening (18).

Initially dramatic differences in arsenic removal were observed when some waters spiked with arsenite were chlorinated before coagulation and others were not. To investigate the effect of chlorine contact time on arsenic removal, experiments were performed on waters containing 0.3 mg/1 of arsenic^{III} and treated with 30 mg/1 of alum. Arsenic^{III} removals in

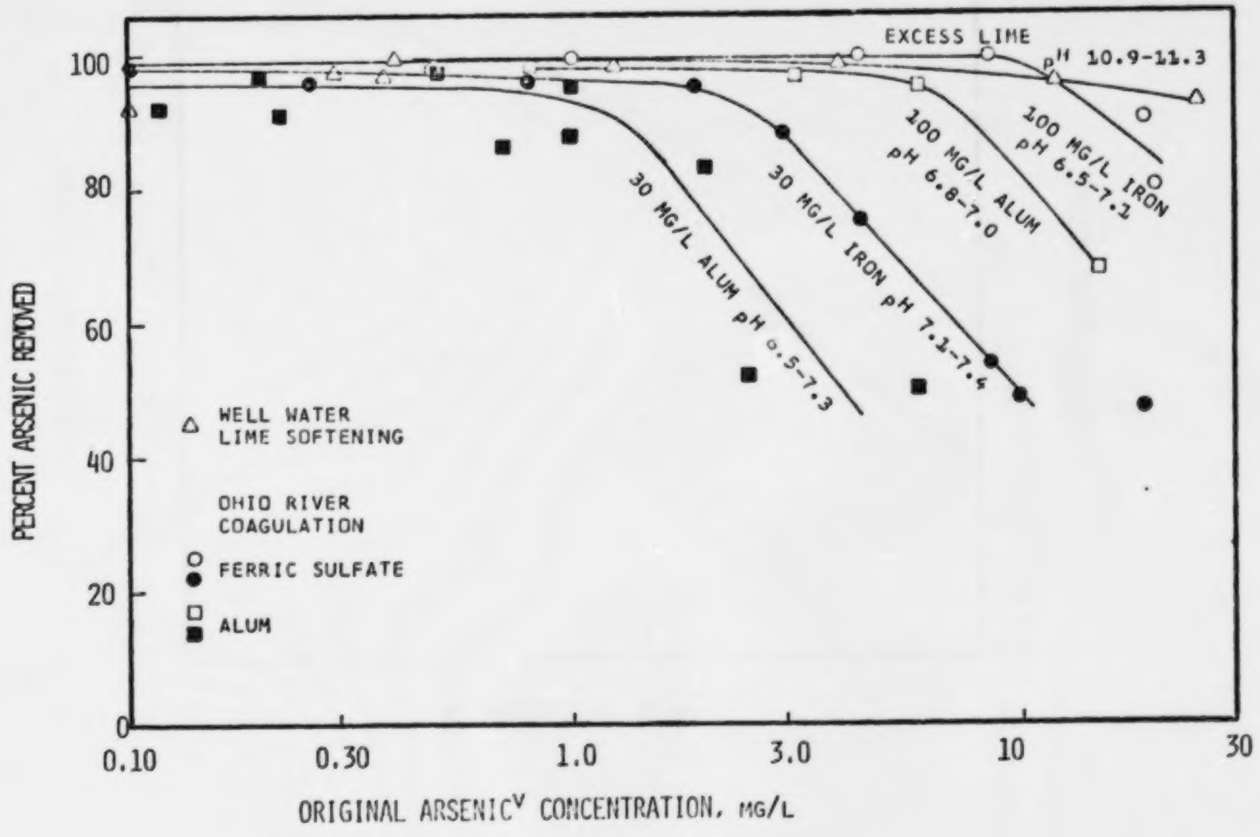


Figure 8. Effect of Arsenic^V Concentration and Treatment Process on Removal.

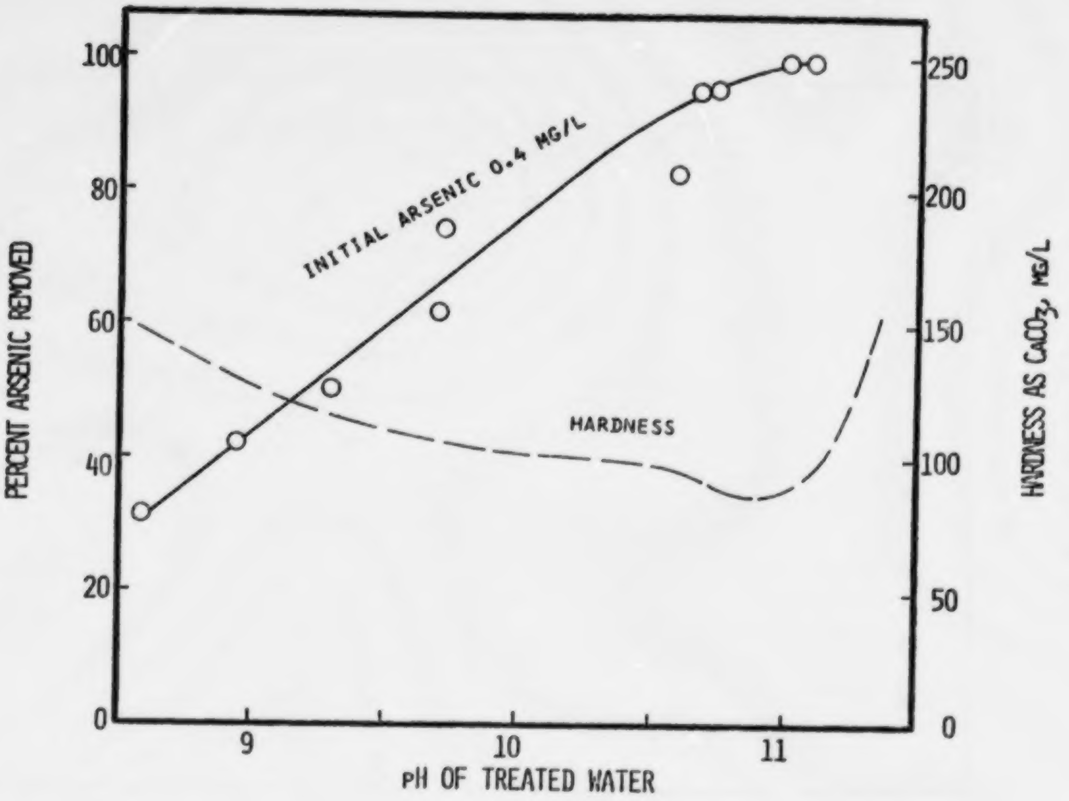


Figure 9. Arsenic^V Removal by Lime Softening.

unchlorinated samples were about 10 percent. The contact time between addition of chlorine (sodium hypochlorite) and the beginning of rapid mix of the coagulant varied from 5 to 120 minutes. Arsenic removals for all contact times from the minimum to the maximum ranged between 50 and 60 percent. After this study, a standard chlorine contact time of 10 minutes was used in subsequent chlorination tests.

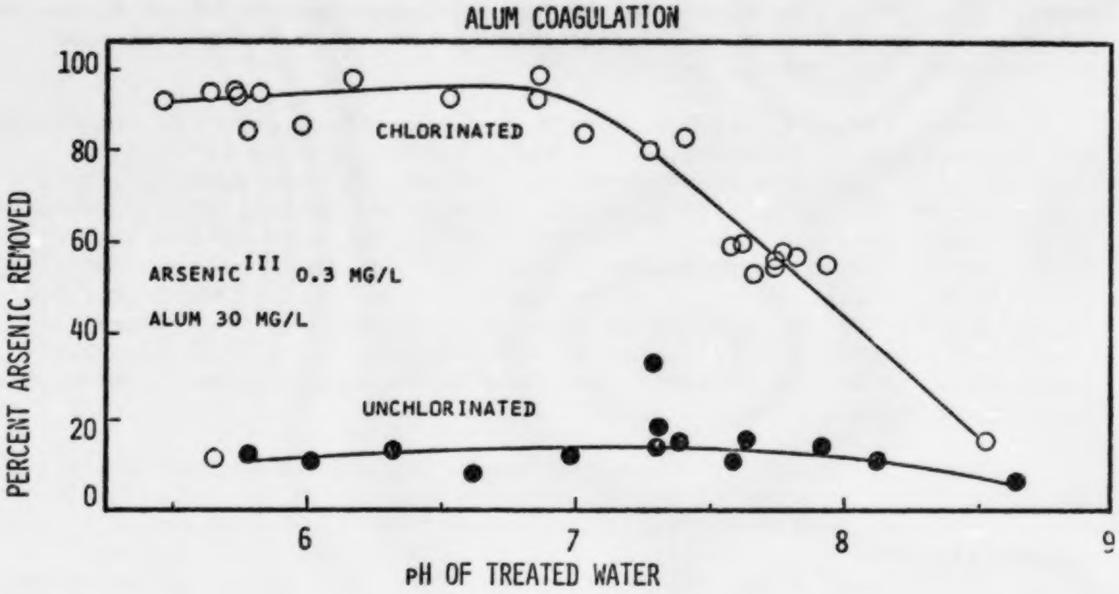
Several variables were considered in the arsenite removal by coagulation experiments: one of these was pH. Arsenite removal by alum and by iron coagulation did not show great variation with pH. Maximum arsenite removals occurred from pH 6 to pH 8 (Figure 10). Experiments dealing with chlorination of arsenic^{III} were also performed. Chlorine residual measurements were made at the end of such tests to ascertain that chlorine demand had been satisfied while still leaving a residual in the treated water. Chlorination produced arsenic removal results similar to those found by Gulledge and O'Connor in studies of arsenic^{V} (5). Arsenic removals decreased above pH 7 with alum coagulation. A decreasing trend also was seen for arsenic removal above pH 8 with ferric sulfate coagulation.

Studies of arsenic^{III} removal by ferric sulfate showed that removals depend on coagulant dose and initial arsenite concentration. Removals increased with higher coagulant doses, but decreased when coagulant dose was held constant and initial arsenite concentration was increased (Figure 11). The most significant factor in the treatment was chlorination, however, Chlorinated water samples dosed with arsenic^{III} showed removals almost identical to earlier results obtained in research with arsenic^{V} (Figure 8).

Arsenic^{III} removal by alum was also investigated. Alum was considerably less effective for arsenite removal than ferric sulfate when samples were not chlorinated (Figure 12). For example, results for coagulation with 30 mg/l of alum were generally 20 percent of less compared with removals in the 40 to 60 percent range for 30 mg/l of ferric sulfate. Again, though, dramatic increases in arsenic removal were observed when waters spiked with arsenite were chlorinated before coagulation. Then the results obtained were similar to previous results with arsenic^{V} (Figure 8).

During precipitative softening, unchlorinated arsenic removal was poor when the pH of the treated water was below 10.5. As the pH approached 11 arsenic removal increased sharply and then leveled off at 70 percent (Figure 13). When waters containing arsenic^{III} were chlorinated and then softened, the results were nearly identical to the previous results obtained for arsenic^{V} removal by softening. In both cases, maximum removal occurred at pH values of 10.7 or above.

Effects of arsenic concentration on removal by softening are shown in Figure 14. Slight decreases in removal of unchlorinated arsenic^{III} occurred as initial concentrations of arsenic^{III} increased from 2 to 10 mg/l. The best removals of unchlorinated arsenic^{III} did not exceed 80 percent. however. In contrast to this removals of chlorinated arsenic^{III} and arsenic^{V} (for comparison) by lime softening to pH values between 10.9 and 11.3 were 95 percent or higher for arsenic concentrations from 0.1 to 10 mg/l.



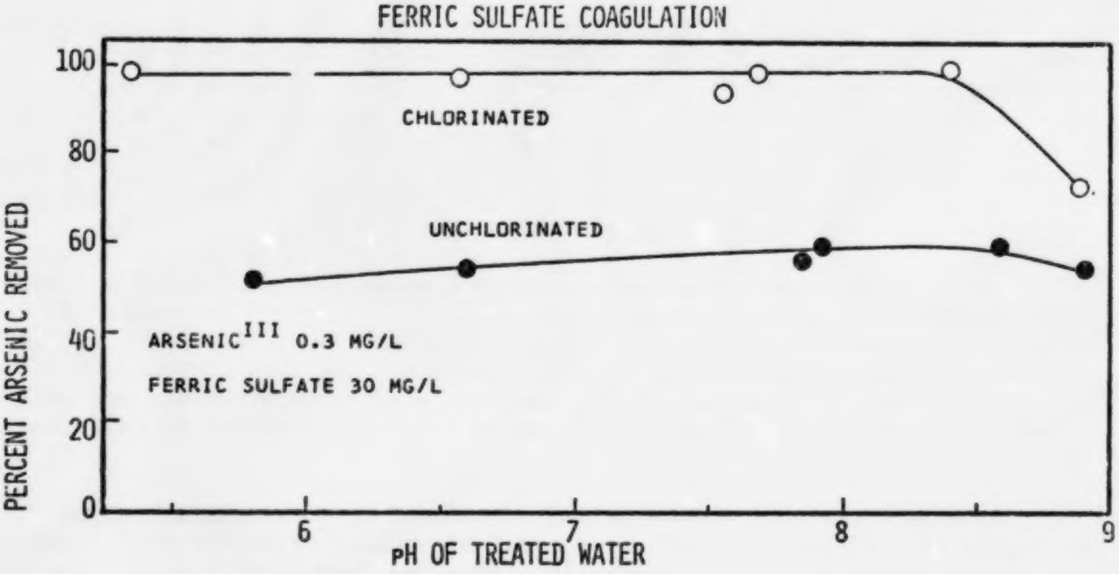


Figure 10. Effect of pH and Chlorination on Arsenic Removal by Coagulation.

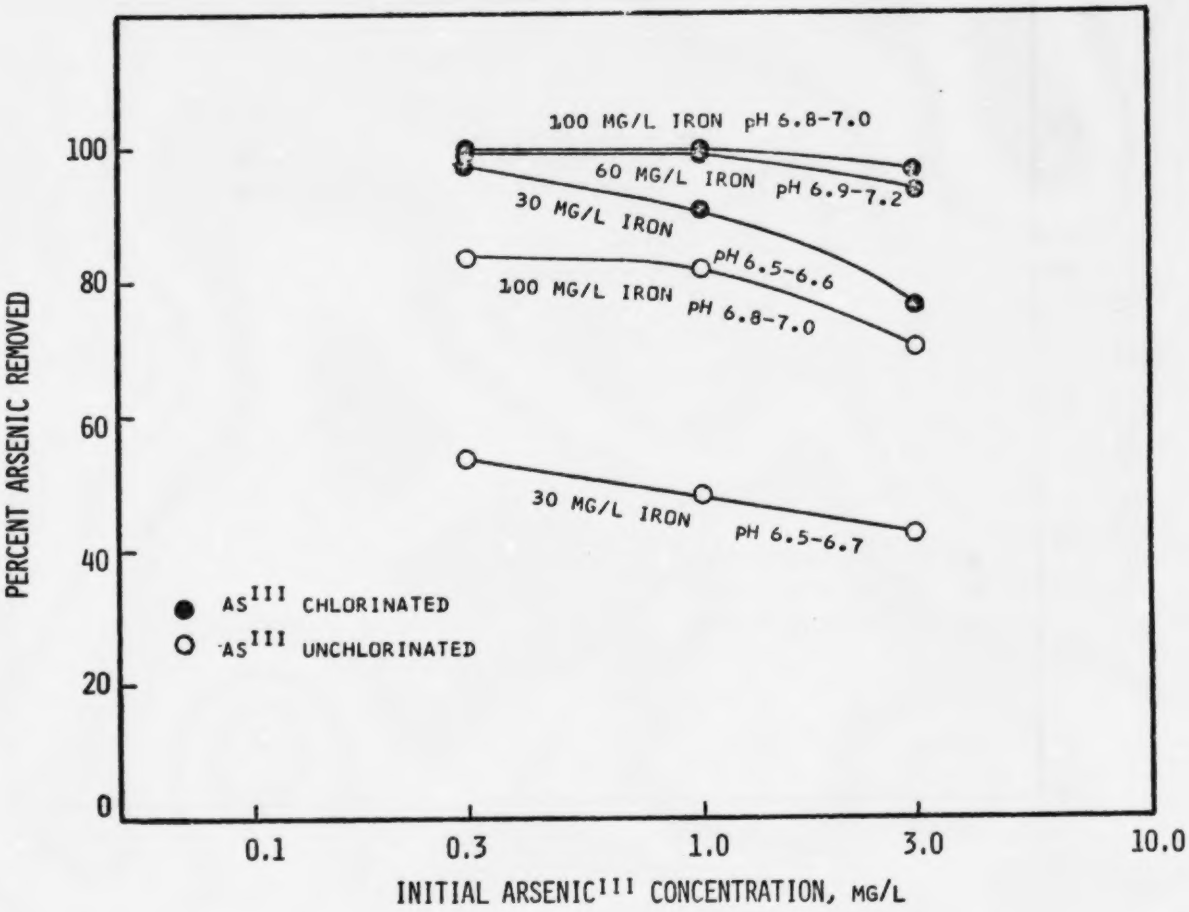


Figure 11. Arsenic Removal by Ferric Sulfate Coagulation.

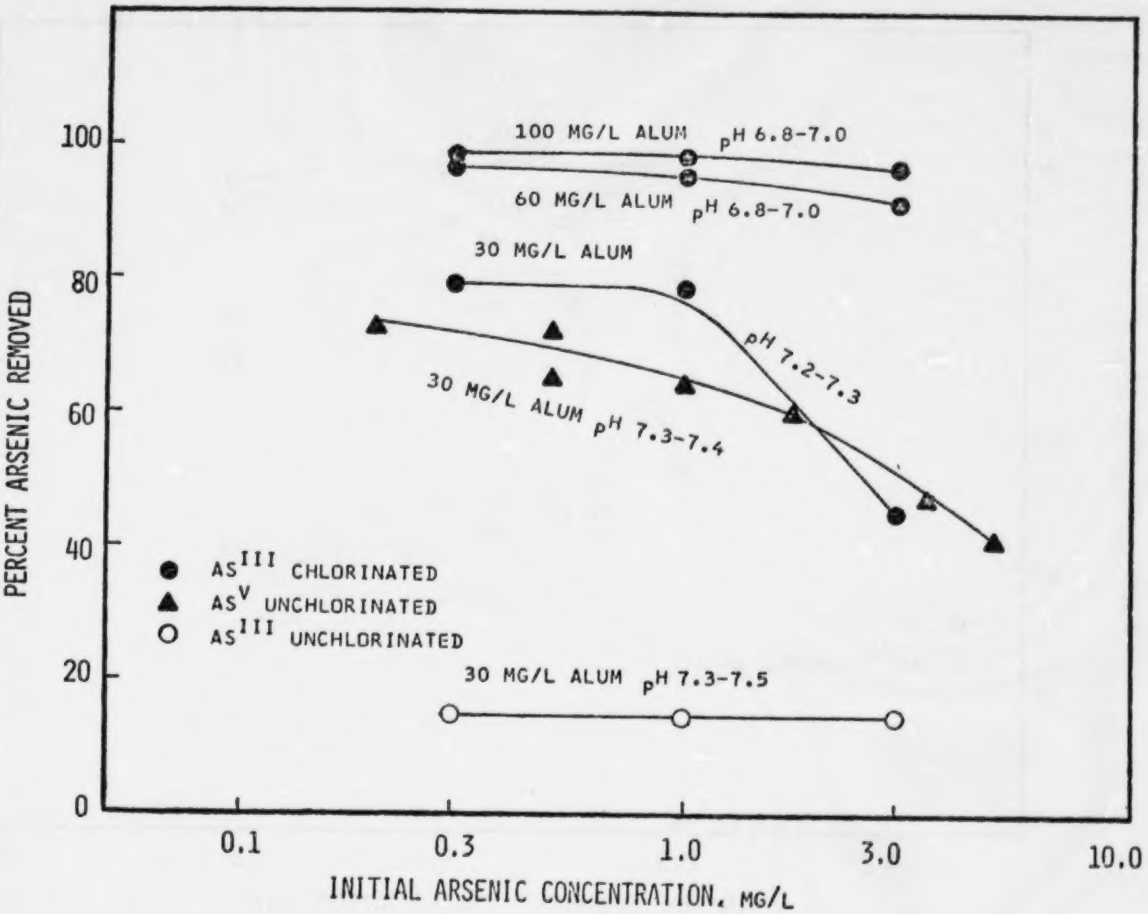


Figure 12. Arsenic Removal by Alum Coagulation.

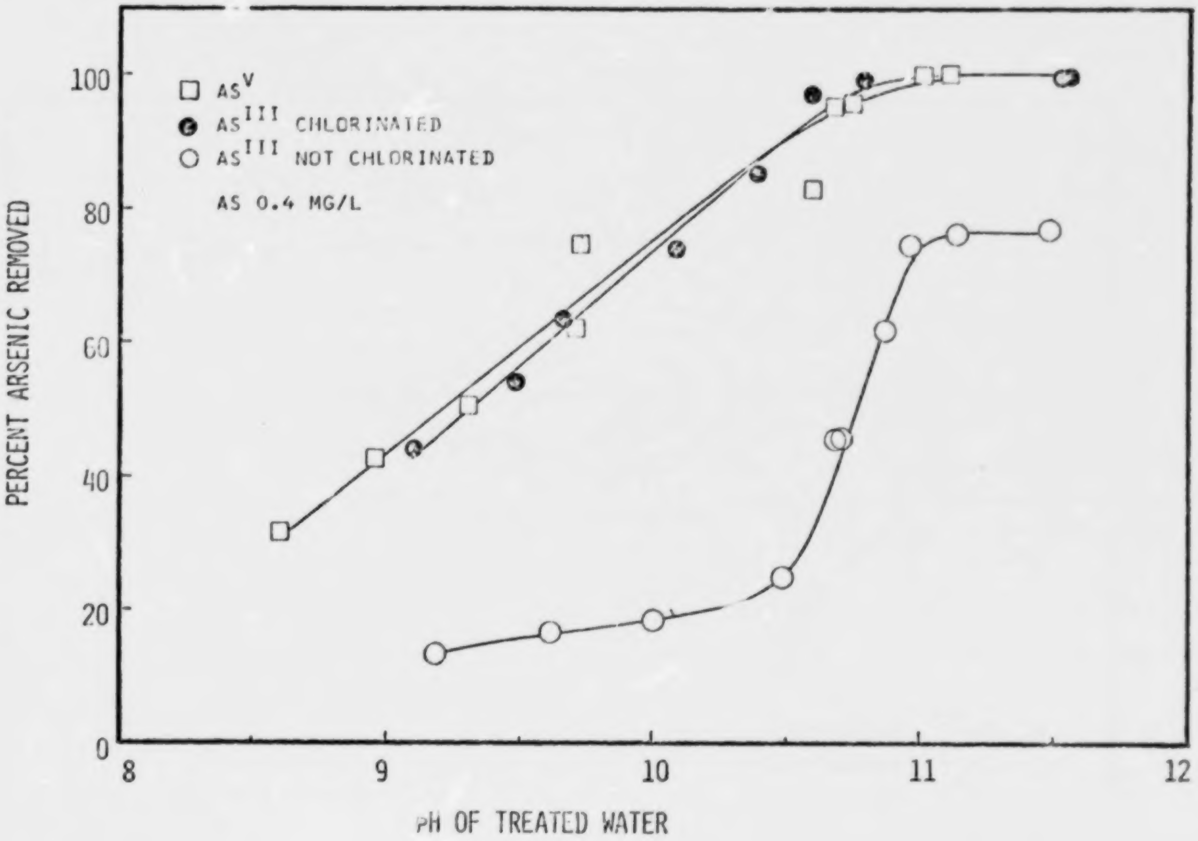


Figure 13. Arsenic Removal by Lime Softening.

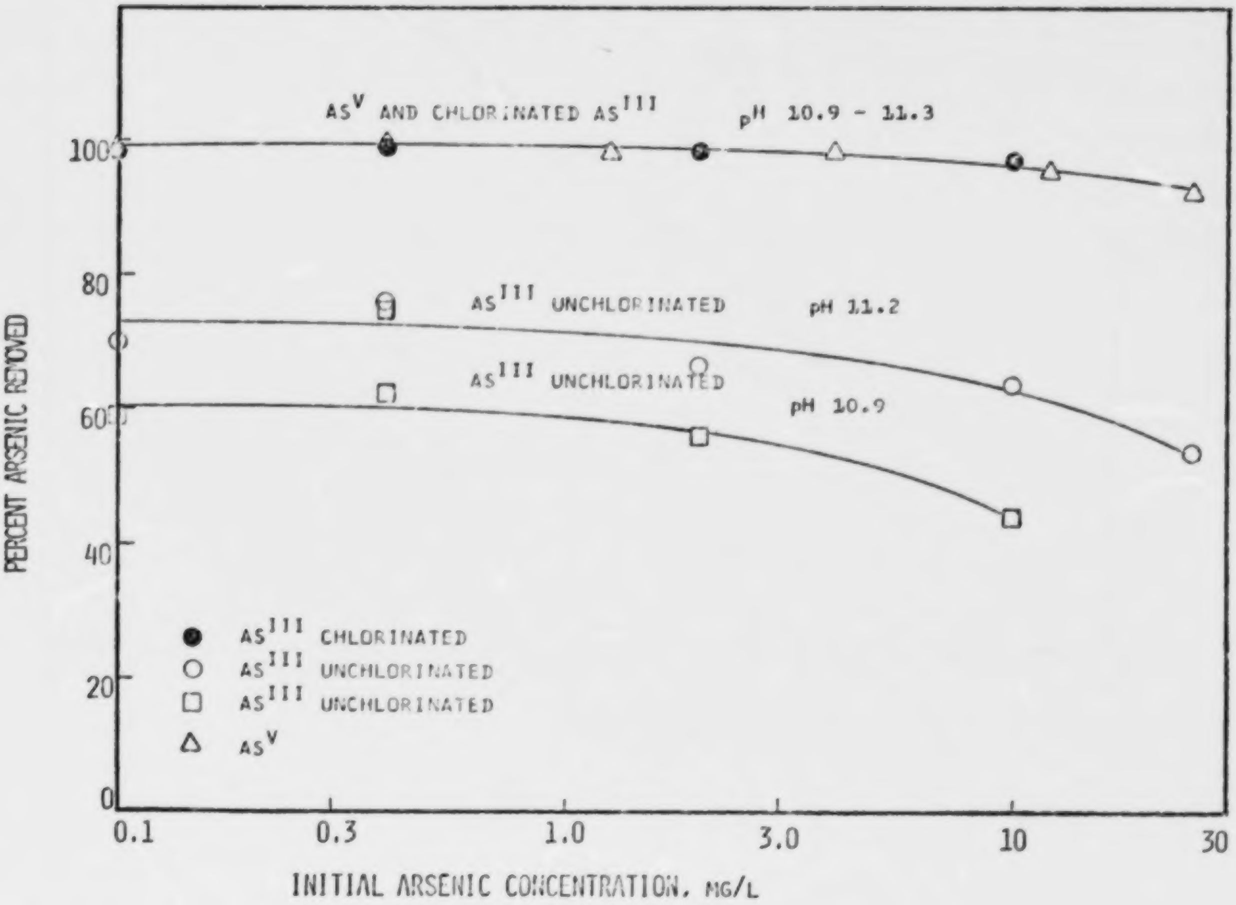


Figure 14. Arsenic Removal by Excess Lime Softening.

Removing arsenic^{III} by powdered activated carbon was attempted. The arsenic concentration used for these studies was 1.0 mg/l. Carbon doses varied from 5 to 300 mg/l. Experiments were conducted at pH values ranging from 6.1 to 8.2. The removals of arsenite were poor; all were less than 10 percent. Because removing arsenic^{V} by activated carbon was also less than 4 percent for the various conditions investigated, no carbon adsorption tests involving chlorination were carried out.

The most significant finding in the research on arsenite removal was that for treatment by coagulation or softening, removal efficiencies will nearly always be significantly improved if the arsenite is oxidized to arsenate before removal is attempted. Although other forms of oxidation, such as treatment with ozone or potassium permanganate, were not attempted, they should also be effective.

This agrees with the work Shen, who found that higher removal efficiencies could be obtained by treatment of groundwater with potassium permanganate or chlorine before coagulation was initiated (6). The groundwater studied in his work exhibited a chlorine demand. All of the chlorine demand of a water should be satisfied to ensure that all the arsenite present in an arsenic-bearing groundwater has been oxidized to the more readily removed arsenate form. When this has been accomplished, arsenic removal should prove less difficult.

Selenium

The behavior of two forms of selenium, selenite (Se^{IV}) and selenate (Se^{VI}), has been studied. Results of selenate removal can be easily summarized -- they were uniformly poor. Selenate removals by coagulation with iron or alum (up to 100 mg/l of coagulant), by softening from pH 9 to 10.8, or by treatment with up to 100 mg/l of powdered activated carbon were less than 10 percent for initial selenate concentrations of 0.1 mg/l as selenium. Coagulation tests were carried out with Ohio River water and also with Glendale well water. This work was done with ^{75}Se and stable carrier. Selenate removal was observed only in the cation-anion exchange column, and this technique is the one studied thus far that merits further investigation.

Because an existing problem of selenium in groundwater had been identified in the Midwest, removal of selenite was investigated primarily with Glendale well water, rather than with Ohio River water. Because substances such as iron and sulfur are found in the reduced state in groundwater, expecting selenium in groundwater to be in an oxidation state no higher than selenium^{IV} seems logical.

Literature had shown that the reaction of selenium with hydrous oxides of iron was quite dependent upon pH (19-22). The reactions of selenite, either coprecipitation with or sorption by hydrous ferric oxides, decreases greatly when pH exceeds 8. Therefore, studies of selenite included pH as a variable.

The results of coagulation experiments are shown in Figures 15 and 16. At a constant ferric sulfate dose and selenium concentration, removal improves as pH decreases, with smaller removal increments as pH decreases from 6 to 5 (Figure 15). Removals also increase with higher coagulant dose, but at low pH values, the improvement that resulted from adding more ferric sulfate was not as great as that obtained at pH 7 or above. Results of alum coagulation (Figure 16) indicate the trends are the same as those observed for iron coagulation. Removals with alum, however, were generally lower than removals with ferric sulfate.

A limited study of coagulation of surface water spiked with selenite was undertaken, and results were similar to those obtained with well water. Selenite removals from Ohio River water with 25 to 100 mg/l of ferric sulfate fell within the limits shown in Figure 15 for pH 7.0 to 7.5. Selenite removals from river water with alum were somewhat higher than removals from well water using alum.

When either selenite or selenate was added to Ohio River water samples with turbidities of up to 65 T.U.s, removals by stirring overnight and then centrifuging for clarification did not exceed 6 percent. Thus sorption of selenium onto natural turbidity at pH 7 to 8 does not seem very likely.

In jar tests with up to 100 mg/l of powdered activated carbon, removals of selenium were less than 4 percent for selenite. Glendale well water was used in carbon adsorption tests in contrast to the coagulated and settled secondary sewage effluent used by Linstedt et al. (9). The finding of poor selenite removal in a water free of organics adds strength to the suggestion that selenite adsorption by activated carbon in the Linstedt et al. research was related to the organic content of the test water.

Removal of selenite by softening was attempted. A slightly increasing trend for removal with increasing pH was observed (Figure 17). Nevertheless, removals did not exceed 40 to 50 percent and generally were lower, so lime softening or excess lime softening would not be recommended for selenium removal.

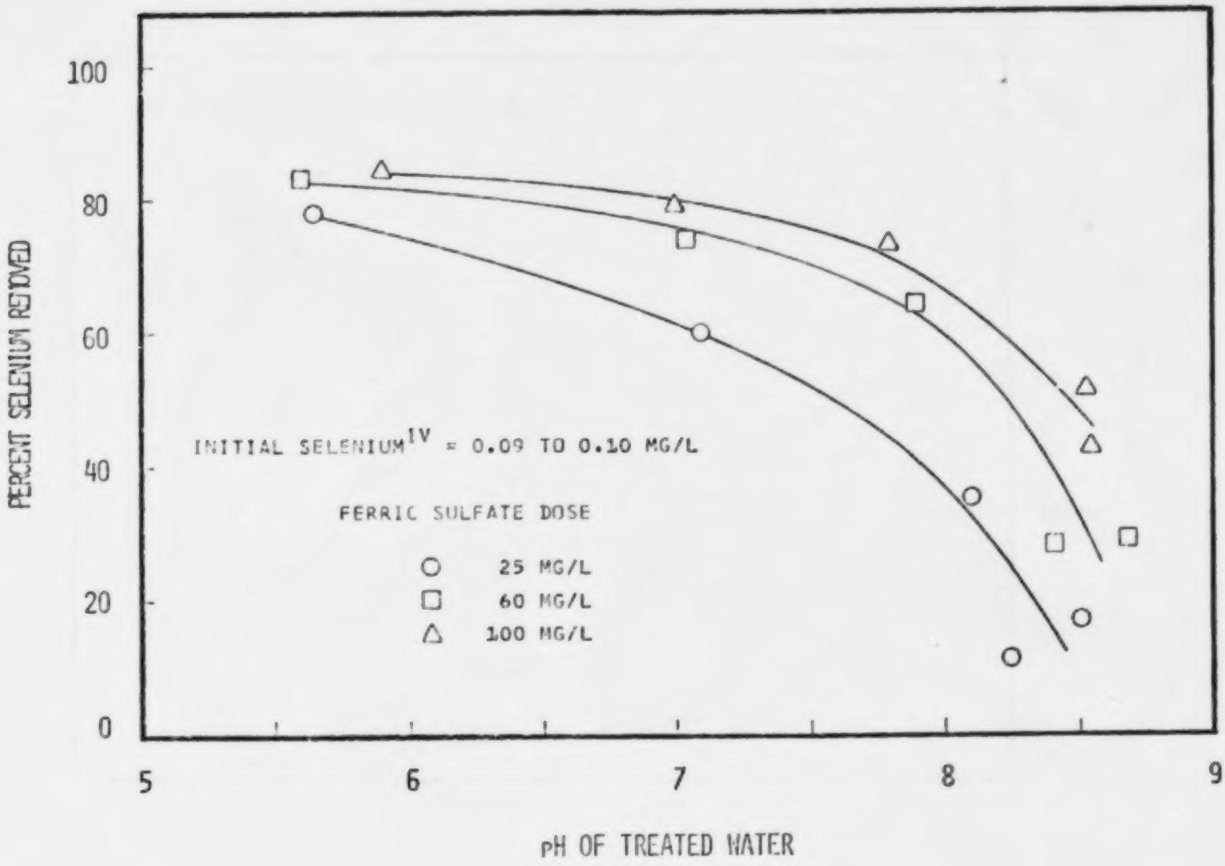


Figure 15. Effect of pH on Selenium Removal by Iron Coagulation.

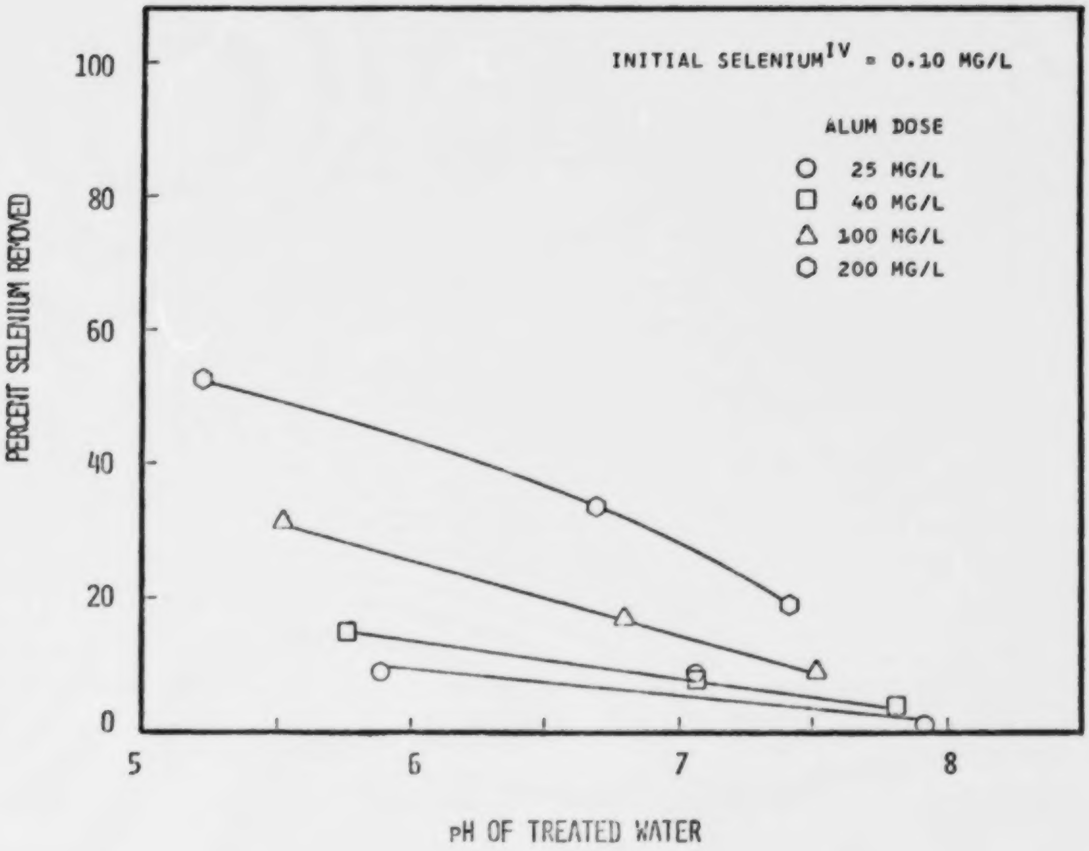


Figure 16. Effect of pH on Selenium Removal by Alum Coagulation.

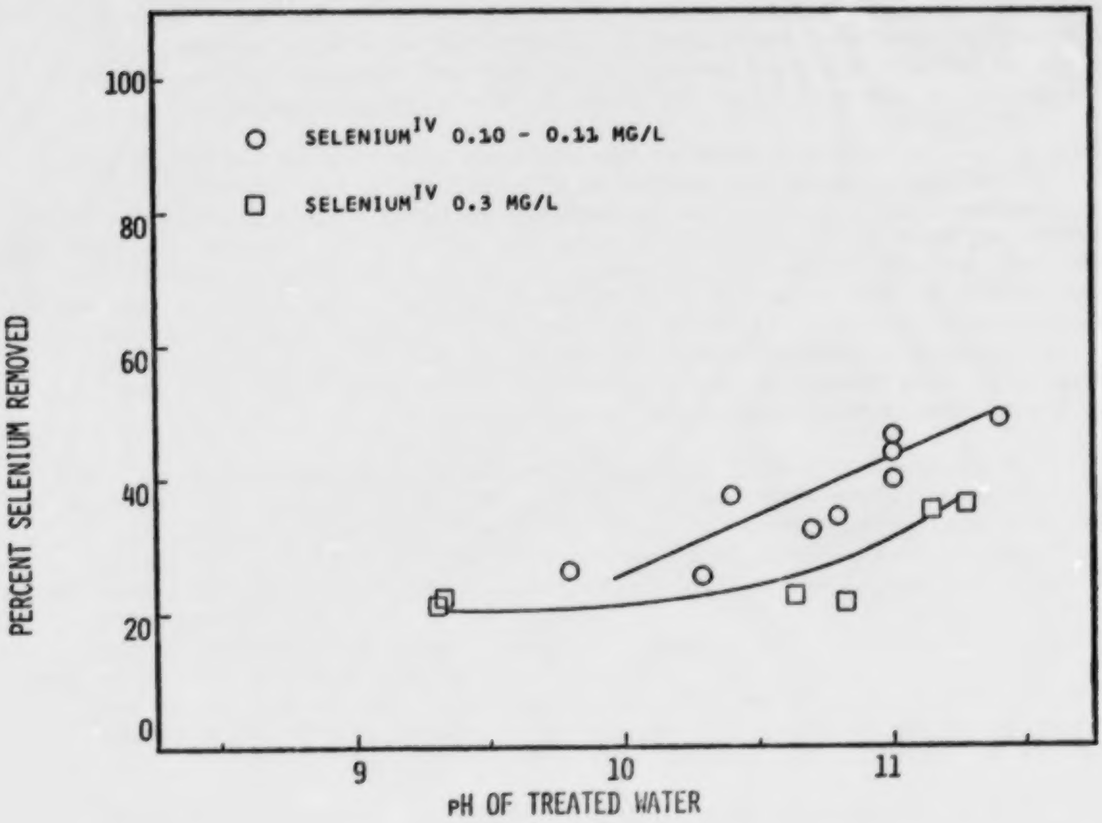


Figure 17. Selenium Removal by Lime Softening.

SUMMARY

The results of research for the removal of inorganic contaminants are summarized in Table I. The data upon which Table I is based are almost entirely the results of bench-scale work. Engineering designs should not be undertaken until these data are verified by pilot plant tests. This work will be useful in selecting processes which might be most fruitfully investigated on a larger scale, however.

Three of the processes listed in Table I were found to be most effective for removal of one or more of the trace inorganics studied: activated carbon, for organic and inorganic mercury; ferric sulfate coagulation, for removal of selenium^{IV}, arsenic^{III}, and arsenic^{V}; excess lime softening, for inorganic mercury, barium, arsenic^{III}, and arsenic^{V}. Note that because efficacy of treatment techniques is categorized in removal ranges, e.g., 60 to 90 percent for good removal, more than one treatment method may be designated as the best means for removal of a given contaminant.

No single treatment process was the most effective or preferred method for all of the contaminants tested so far (See Table I). Therefore, no one treatment technique can be recommended as being always preferred. The design engineer must carefully consider the water to be treated, its chemical content, and any characteristics about its source that might suggest the possibility of contamination with trace inorganics. For instance, the natural occurrence of arsenic, selenium, and barium in certain geographical areas of the country should influence the design of facilities in those areas. Because of differences in the treatability of selenium^{IV} and selenium^{VI} treatment should be attempted before oxidation.

Agreement of this work with previous research is generally good. With one exception, there were not serious contradictions of previous findings. The very negligible removal of selenite by activated carbon adsorption contrasted with the findings of Linstedt et al. (9). They explained the somewhat unexpected adsorption of inorganic selenium by suggesting that the selenium was first associated with organic matter that was subsequently adsorbed on carbon. This explanation appears reasonable because in this work with low-organic-content well water, selenium adsorption was quite poor. The differences in selenium removal in wastewater and in well water call attention to the necessity of doing water treatment studies with waters similar to potable water sources rather than with waste waters.

Of the substances studied thus far (with the exception of selenium^{VI}), if the limits in the Drinking Water Standards are not exceeded by a factor of more than 3 to 5, some conventional treatment method exists that should be adequate to reduce the concentrations below the limits set in the proposed Drinking Water Standards.

TABLE 1. SUMMARY OF JAR-TEST RESULTS OF TREATMENT PROCESSES TO REMOVE TRACE METALS FROM DRINKING WATER

Trace Metal	Alum	Ferric Sulfate	Lime pH 9.5-10	Excess Lime pH 10.6-11	Activated Carbon
Mercury-Organic CH_3HgCl	Poor*	Poor	Poor	Poor	Good**
Mercury-Inorganic $HgCl_2$	Poor	Fair	Fair	Good**	Good
Ba^{++}	Poor	Poor	Good	Good to very good**	Poor
				Zeolite field data - very good**	
Selenium-Inorganic Se^{+4}	Poor pH <7	Fair to good pH <7	Poor	Fair	Poor
Selenium-Inorganic Se^{+6}	Poor	Poor	Poor	Poor	Poor
Arsenic-Inorganic As^{+3}	Poor	Fair to Good**	Poor	Good**	Poor
Arsenic-Inorganic As^{+5}	Good to very good pH *(5)	Good to** very good pH 8(5)	Good	Very good**	Poor

*Key- Poor = 0 - 30% removal
Fair = 30 - 60% removal
Good = 60 - 90% removal
Very good = Above 90% removal

**Best treatment technique.

Acknowledgment

The authors wish to acknowledge the laboratory assistance of Bradford Smith and Charles Donovan and the participation of Thomas Sorg in portions of this work.

Figures 1,2,3,4,8,9,15,16 and 17 appeared in "Removal of Trace Inorganics by Drinking Water Treatment Unit Processes," by G. S. Logsdon and J.M. Symons, published in Water 1973. These figures are reproduced with the permission of the American Institute of Chemical Engineers.

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9-17-73

REMOVAL OF HEAVY METALS FROM WASTEWATER WITH STARCH XANTHATE

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Princeton, New Jersey

Session IV

Foam Fractionation, Solvent Extraction
and Other Processes

November 16, 1973

Introduction

Worldwide concern developed a few years ago when people became aware of the effect of discharging industrial effluents containing heavy metals into waterways. This led to the formation of a set of strict discharge limits for heavy metals that must be met before industrial effluents can be discharged. Several methods have been developed and are being used to treat these industrial effluents contaminated with heavy metals (Figure 1). Each of these methods has advantages but most have disadvantages requiring special modifications before use by certain industries.

The method developed at the Northern Regional Research Laboratory in Peoria offers industry a tool to remove heavy metals in most cases to concentrations below discharge limits.

Description of Method

Our method involves the sequential addition of starch xanthate and a cationic polymer [e.g., poly(vinylbenzyltrimethylammonium chloride) (PVBTMAC) or polyethylenimine (PEI)] to a heavy metal solution to precipitate both polymers and the heavy metals as a cohesive floc (Figure 2). Some of the xanthate groups on the starch backbone form heavy metal salts, while others react with the polycation to form an insoluble polyelectrolyte complex.

The overall process (Figure 3) involves precipitation, separation and recovery. Once the precipitate forms it settles rapidly and separation may be achieved by filtration, centrifugation or decantation. The resulting sludge can then be treated with acid or incinerated to recover the metal.

Variables Investigated

Several variables were evaluated to optimize heavy metal removal. Mercury was selected as the metal used in this evaluation; however most heavy metals give similar results.

A. End-Point Determination. Solutions containing mercury and cationic polymer were titrated with 1% solutions of starch xanthate. The amount of xanthate required to give maximum precipitation of the cationic polymer and mercury was determined by streaming current measurements. Figure 4 shows a typical titration curve for this precipitation. Figure 5 shows how critical the amount of starch xanthate added is for the optimal removal of mercury. An excess of starch xanthate causes an imbalance between the polyelectrolytes and some mercury xanthate complex redissolves.

B. Concentration of Cationic Polymer. The optimum amount of cationic polymer was determined for various concentrations of mercury. For a 100 ppm solution of mercury, 0.46 g/l. PVBTMAC should be used to obtain a minimum residual mercury concentration.

C. Rate of Starch Xanthate Addition. The slower the starch xanthate is added the more effectively it complexes with mercury. Therefore complexation is probably not an instantaneous reaction. Slow precipitation does produce fewer and larger particles, which are more easily filtered.

D. Presence of Salt (NaCl). The method is effective if the salt (NaCl) concentration is below 3%. Increasing salt concentrations above 3% slightly lowers the effectiveness of the method.

E. Presence of Sequestrants. The presence of selected sequestrants at the 0.1 g/l. level does not affect removal of mercury (Table I).

F. Effect of Initial pH. Treatment of mercury solutions having initial pH's of 3-11 result in low residual mercury concentrations. Solutions with pH's of less than 3 cause rapid decomposition of the starch xanthate.

G. Other Variables. 1. Degree of substitution (DS) of starch xanthate--Starch xanthates having DS from 0.11 to 0.40 were effective for removing mercury. Smaller addition volumes were required as the DS of the starch xanthate increased.

2. Order of addition of the polymers--The starch xanthate and cationic polymer can be added in either order for effective removal.

3. Omitting cationic polymer--Starch xanthate can react with mercury in the absence of cationic polymer to form a precipitate. However, this method was only effective for high mercury concentrations (100 mg/l.) and still left residual mercury above 100 μg/l.

Residual Contaminants

Any process for removing heavy metals from water should not add other noxious substances. Contaminants that might be introduced by treatment of water with starch xanthate and a cationic polymer include: small ionic species (Cl^- from the cationic polymer; Na^+, OH^- and $CS_3^=$ from the xanthate), small nonionic species (CS_2 and COS from the xanthate), and the polyelectrolytes themselves. The residual concentrations found [chloride, 200 mg/l. and sulfur (reported as sulfate), 36 mg/l.] and the BOD_5 (0-12.5 mg/l.) were well below established limits. Therefore, precipitation of heavy metals with starch xanthate and cationic polyelectrolytes does not appear, in itself, to produce legally unacceptable concentrations of these residual contaminants for which limits have been established.

Removal of Other Heavy Metals

Tables 2 and 3 show the effectiveness of removal of 10 metals tested using the starch xanthate-cationic polymer method. For comparison similar metal solutions were treated with sodium hydroxide to precipitate the metals as their hydroxides. The tables also list the solubility product constants for the metal ethyl xanthates. The constants are useful in determining how effectively the metal will be removed with the starch system.

Scale-Up

The method has been scaled-up to 25 gallons of metal solution. Table 4 shows the concentrations of residual metal.

Testing of Other Cationics

Several cationic polymers have been evaluated. Table 5 compares the effectiveness of several polymers ranging in price from $0.13 to $1.50 per pound.

Advantages of the Method

Several important advantages of the starch xanthate-PVBTMAC method are apparent. Metal recovery for reuse is possible with mild acid treatment of the complex. The volume of sludge to be treated for recovery of the metal or to be disposed of is small compared to that obtained from several other processes. The physical nature of the sludge is not gelatinous as with usual basic precipitation and the floc settles faster and can be removed easier. Some methods require the removal of suspended solids before treatment; however, this is not necessary with the xanthate method. The starch xanthate method is effective over a pH range of 3-11.

Additional Information

In the previous discussion it was shown that the fairly expensive cationic polymer was necessary for effective removal. Recently, the process has been modified to eliminate the cationic polymer and utilize only starch xanthate to effect heavy metal removal.

The starch xanthate in this modified process is water insoluble. Figure 6 gives a scheme for the preparation and use of this product.

Table 6 shows the effectiveness of solid starch xanthate in removing heavy metals from water. The solid starch xanthate is basic so the pH of the solution will increase. Effective removal is always obtained in the pH range of acceptable discharge. A contact time of as little as 5 min is sufficient for good removal. For example, a solution containing 31,770 μg/l. Cu^{+2} was reduced to a residual level of 22 μg/l. Cu^{+2} with 5 min contact time and to a level of 20 μg/l. with 120 min. Low residual metal concentrations were obtained with varous DS solid starch xanthates; however the higher the DS, the greater the metal binding capacity assuming one metal ion per one xanthate group.

Metal release from the product using nitric acid is effective and the metal is recovered as a concentrated metal solution. The xanthate is oxidized by the acid to sulfate and the insoluble starch is recovered for rexanthation and reuse.

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"Removal of Heavy Metal Ions from Wastewater with a Starch Xanthate-Cationic Polymer Complex," R. E. Wing, C. L. Swanson, W. M. Doane and C. R. Russell, J. Water Pollut. Contr. Fed. (submitted).

"Insoluble Starch Xanthate: Preparation and Use in Heavy Metal Recovery," R. E. Wing (correspondence aid).

TABLE 1.--Effect of Sequestrants on Residual Mercury Level and Starch Xanthate Requirement[1]

Sequestrant[2]	Residual Mercury (μg/1.)	Xanthate Requirement (meq X 10^2)
Diglycolate	4.37	5.61
Nitrilotriacetic acid	3.86	5.19
Polyphosphate	10.3	3.36
Citrate	10.33	4.36
Control	6.1	6.53

[1] Meq of starch xanthate [1% w/v, 0.23 degree of substitution (DS)] required to precipitate 2.5 X 10^{-2} mM (5 mg) mercury(II) and 4.74 X 10^{-2} meq poly(vinylbenzyltrimethylammonium chloride) (PVBTMAC) from 50 ml of solution.

[2] In each 50-ml test solution 5 mg of sequestrant was used. The control contained none.

TABLE 2.--Heavy Metal Removal from Solutions of Individual Metals by Treatment with Starch Xanthate-PVBTMAC[1] (Final pH 7) vs. Sodium Hydroxide (pH 7 and 9)

Metal	Treatment[2]	Starch-Xan[3] (ml)	Initial pH	Initial Concn. (µg/l)	Residual Concn. (µg/l)	Illinois Limit[4] (µg/l)	pH, Optimum for Hydroxide Precipitation	K_{sp}, Metal Ethyl Xanthate[5]
Cadmium(II)	Xan-PVBTMAC	4.65	3.1[6]	56,200	8	50	6.7[7]	2.6×10^{-14}
	NaOH (pH 7[8])		2.9	56,200	29,600			
	NaOH (pH 9)		2.9	56,200	4,500			
Chromium(III)	Xan-PVBTMAC	3.45	4.5[6]	26,000	52	1,000	5.3[7]	---
	NaOH (pH 7)		3.0	26,000	3,800			
	NaOH (pH 9)		3.0	26,000	416			
Copper(II)	Xan-PVBTMAC	4.50	3.0[6]	31,770	12	20	5.3[7]	5.2×10^{-20}
	NaOH (pH 7)		2.9	31,770	1,100			
	NaOH (pH 9)		2.9	31,770	24			
Iron(II)	Xan-PVBTMAC	3.40	3.7[6]	27,920	2,980	1,000	5.5[7]	8.0×10^{-8}
	NaOH (pH 7)		2.6	27,920	2,920			
	NaOH (pH 9)		2.5	27,920	14,500			
Iron(III)	Xan-PVBTMAC	3.70	3.65	27,920	890	1,000	2.0[7]	---
	NaOH (pH 7)		3.65	27,920	146			
	NaOH (pH 9)		3.65	27,920	15			
Lead(II)	Xan-PVBTMAC	4.60	3.1[6]	103,600	8	100	6.0[7]	2×10^{-17}
	NaOH (pH 7)		3.0	103,600	34,500			
	NaOH (pH 9)		3.0	103,600	8			
Manganese(II)	Xan-PVBTMAC	4.10	3.2[6]	27,470	10,700	1,000	8.5[7]	10^{+2}
	NaOH (pH 7)		3.0	27,470	10,700			
	NaOH (pH 9)		3.0	27,470	9,600			
Mercury(II)	Xan-PVBTMAC	4.70	3.2	100,000	3.8	0.5	7.3[7]	1.7×10^{-38}
	NaOH (pH 7)		3.2	100,000	>10,000			
	NaOH (pH 9)		3.2	100,000	8,140			
Nickel(II)	Xan-PVBTMAC	4.15	3.3[6]	29,350	275	1,000	6.7[9]	1.4×10^{-12}
	NaOH (pH 7)		3.2	29,350	5,820			
	NaOH (pH 9)		3.2	29,350	4,350			
Silver(I)	Xan-PVBTMAC	4.52	3.2	53,935	3	5	9.0[9]	5×10^{-19}
	NaOH (pH 7)		3.2	53,935	15,800			
	NaOH (pH 9)		3.2	53,935	14,800			
Zinc(II)	Xan-PVBTMAC	4.10	3.6[6]	32,680	3,300	1,000	7.0[7]	4.9×10^{-9}
	NaOH (pH 7)		3.3	32,680	6,900			
	NaOH (pH 9)		3.3	32,680	1,010			

[1] PVBTMAC at 1 percent concn.

[2] Stock metal solution (2.5 ml) + distilled water (47.5 ml).

[3] Starch xanthate (xan) (DS 0.23) required to reach maximum precipitation of stock metal solution (2.5 ml) + distilled water (47.5 ml) at pH 7, after PVBTMAC (1 ml) is added.

[4] State of Illinois discharge limits for public and food processing waters [Illinois Pollution Control Board, Newsletter No. 44, p. 7 (Mar. 1972)].

[5] Kakovsky, I. A., "Physicochemical Properties of Some Flotation Reagents and Their Salts with Ions of Heavy Non-Ferrous Metals." Proc. Int. Congr. Surface Activ. 2nd, 4, 225 (1957).

[6] Increase in pH over stock metal solution (2.5 ml) + distilled water (47.5 ml) so final solution after treatment would have a pH of 7.0.

[7] Dean, J. G., et al., "Removing Heavy Metals from Waste Water." Environ. Sci. Technol., 6(6), 518 (1972).

[8] pH 7 or pH 9 = addition of 0.1N NaOH to stock metal solution (2.5 ml) + distilled water (47.5 ml) to reach final pH of 7 or 9.

[9] Diehl, H., and Smith, G. F., "Quantitative Analysis." John Wiley & Sons, Inc., New York, N.Y. (1952).

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TABLE 3.--Heavy Metal Removal From Solutions Containing a Mixture of Them by Treatment with Starch Xanthate-PVBTMAC (Final pH of 7) vs. Sodium Hydroxide (pH 7 and 9)

Treatment	Sample[1] (µg/l)									
	Cadmium(II)	Chromium(III)	Copper(II)	Iron(II and III)	Lead(II)	Manganese(II)	Mercury(II)	Nickel(II)	Silver(I)	Zinc(II)
None	5,620	2,600	3,177	5,484	10,360	2,747	10,000	2,935	5,394	3,268
Xan-PVBTMAC[2]	3	21	16	990	8	1,510	3.8	57	5	319
NaOH (pH 7)[3]	2,978	42	151	79	180	1,508	4,580	1,610	93	1,800
NaOH (pH 9)	390	31	20	34	8	833	4,275	681	62	53
Illinois limit[4]	50	1,000	20	1,000	100	1,000	0.5	1,000	5	1,000

[1] Sample contains 0.25 ml of all stock solutions of metals and 47.5 ml distilled water.

[2] Starch xanthate (0.23 DS) and PVBTMAC (1 ml).

[3] Samples were treated with 0.1N NaOH to attain pH 7 or 9.

[4] Table 2, footnote 4.

TABLE 4.--Heavy Metal Removal from 25 Gallons of Solution by Treatment with Starch Xanthate-Polyethylenimine (PEI)

Treatment	Metal (ppb)							
	Cd^{+2}	Cr^{+3}	Cu^{+2}	Fe^{+2}	Pb^{+2}	Hg^{+2}	Ni^{+2}	Ag^{+1}
None	5,620	2,600	3,177	5,484	10,360	10,000	2,935	5,394
St-xan-PEI[1]	27	22	3	100	8	2	77	3
Illinois limit	50	1,000	20	1,000	100	0.5	1,000	5

[1] Starch xanthate (0.23 DS) - 79.6 g (d.b.) and PEI (Montrek 1000) - 18.9 g (d.b.).

TABLE 5.--Evaluation of Several Cationic Polymers with Starch Xanthate for Removing Heavy Metals

Treatment	Metal (ppb)[1]									
	Cd^{+2}	Cr^{+3}	Cu^{+2}	Fe^{+2}	Pb^{+2}	Mn^{+2}	Hg^{+2}	Ni^{+2}	Ag^{+1}	Zn^{+2}
None	3,620	2,600	3,177	5,484	10,360	2,747	10,000	2,935	5,394	3,268
St-xan-PVBTMAC[2]	7	0	3	66	8	1,179	3.6	45	3	73
St-xan-PEI[3]	35	11	2	42	8	83	Tr	135	3	67
St-xan-CPA[4]	10	0	1	50	8	1,093	Tr	61	5	77
St-xan-CSt-1[5]	30	44	6	583	8	1,083	Tr	338	5	1,037
St-xan-CSt-2[6]	83	11	15	92	8	833	Tr	354	8	210
St-xan-AEWF[7]	26	0	6	100	8	1,083	Tr	69	13	73
Illinois limit	50	1,000	20	1,000	100	1,000	0.5	1,000	5	1,000

[1] Metal concentration determined by atomic absorption with a Varian Techtron AA120 spectrophotometer.

[2] PVBTMAC, 0.2 g/1.; st-xan, 0.78 g/1.

[3] PEI, 0.2 g/1.; st-xan, 0.84 g/1.

[4] CPA (a commercial cationic polyacrylamide, Reten 220), 0.2 g/1.; st-xan, 0.34 g/1.

[5] CSt-1 (a commercial cationic starch, "Cato 8"), 0.4 g/1.; st-xan, 0.26 g/1.

[6] CSt-2 (a commercial cationic starch, "Cato 15"), 0.4 g/1.; st-xan, 0.28 g/1.

[7] AEWF (aminoethylated wheat flour), 0.4 g/1.; st-xan, 0.34 g/1.

TABLE 6.--Removal of Heavy Metals with Insoluble Starch Xanthate

Metal	Initial[1] Concn. (µg/1.)	pH (Initial)	pH[2] (2 h)	Residual Metal (µg/1.)	Illinois Discharge Limit (µg/1.)
Cu^{+2}	31,770	3.4	6.4	7	20
Ni^{+2}	29,350	3.2	7.7	19	1,000
Cd^{+2}	56,200	3.0	6.8	9	50
Pb^{+2}	103,600	3.1	7.3	25	100
Cr^{+3}	26,000	3.2	6.5	3	1,000
Ag^{+}	53,935	3.1	7.2	245	5
Zn^{+2}	32,680	3.1	7.5	46	1,000
Fe^{+2}	27,920	3.0	6.4	0	1,000
Mn^{+2}	27,470	3.3	9.0	1,628	1,000
Hg^{+2}	100,000	3.1	4.2	3	0.5

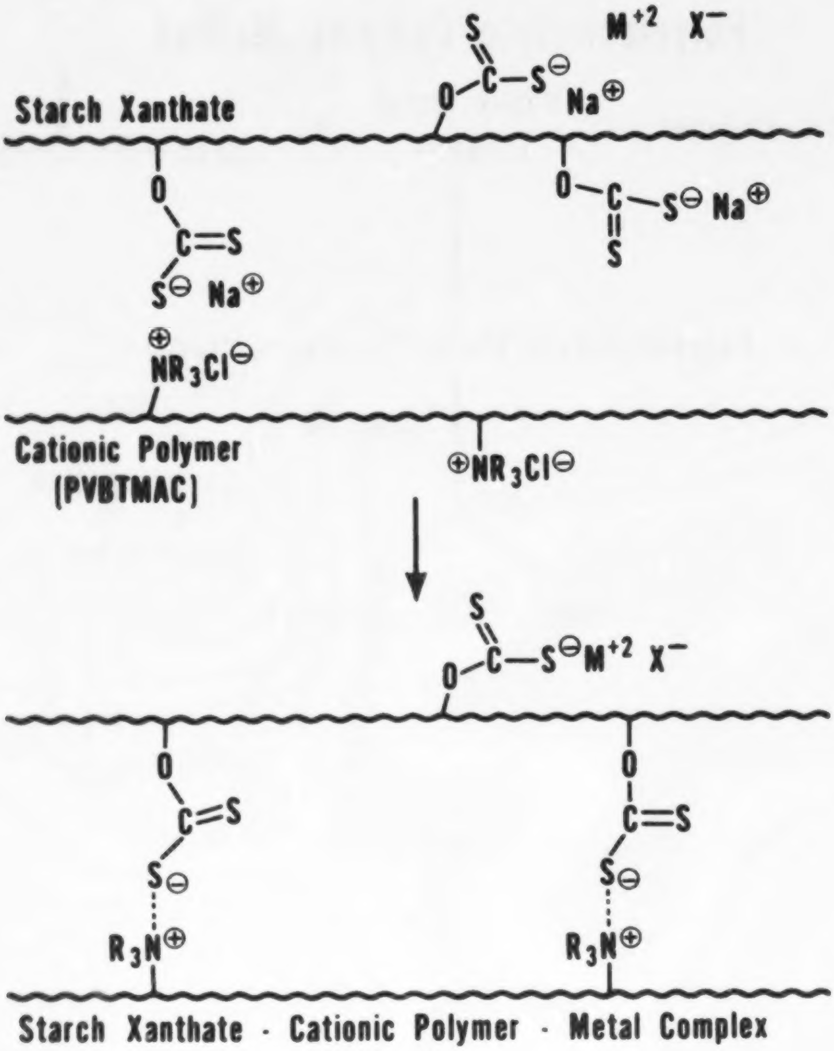
[1] 50-ml sample.

[2] Stir solution 2 h before filtering.

Common Methods Used for Heavy Metal Removal by Industry

1. Chemical Precipitation
    a. Lime
    b. Alum
    c. Iron salts
2. Chemical Treatment
    a. Oxidation
    b. Reduction
3. Ion Exchange
4. Ultrafiltration
5. Electrochemical
6. Evaporative Recovery

Figure 1. Common methods used for heavy metal removal by industry.



Starch Xanthate - Cationic Polymer - Metal Complex Formation

Starch Xanthate
S
M+2 X−
O–C–S⊖
Na⊕
O–C–S⊖ Na⊕
S
O
C=S
S⊖ Na⊕
⊕NR3Cl⊖
Cationic Polymer
(PVBTMAC)
⊕NR3Cl⊖
S
O–C–S⊖M+2 X−
O
C=S
S⊖
R3N⊕
Starch Xanthate - Cationic Polymer - Metal Complex

Figure 2. Starch xanthate-cationic polymer-metal complex.

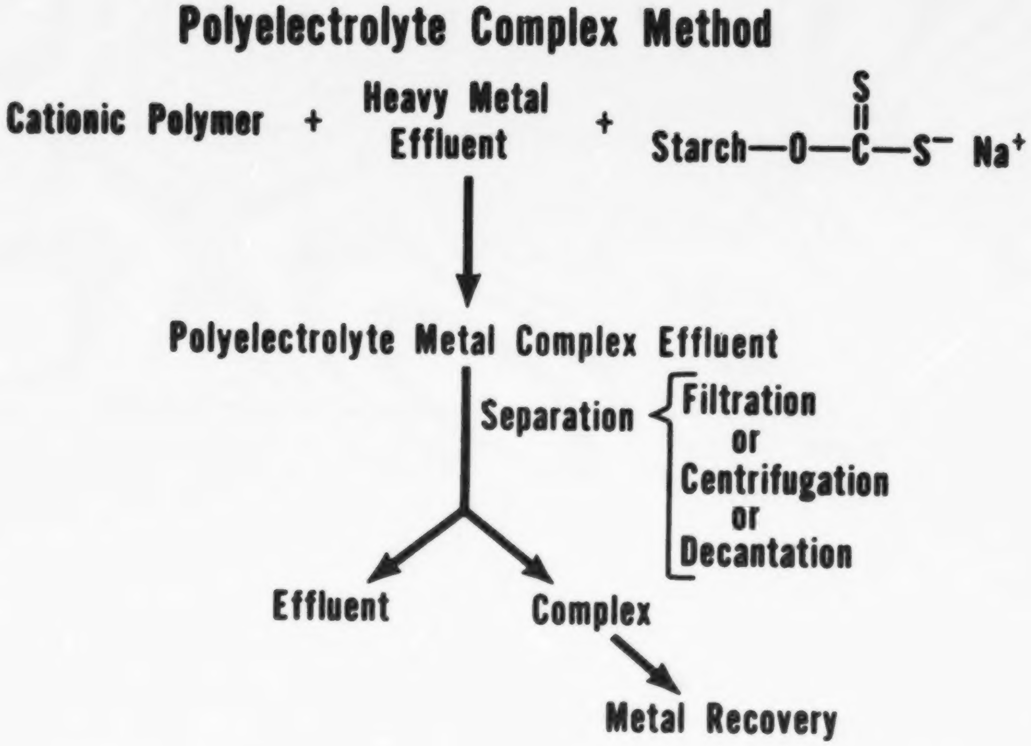

Polyelectrolyte Complex Method
Cationic Polymer
+
Heavy Metal Effluent
+
Starch—O—C(=S)—S⁻ Na⁺
Polyelectrolyte Metal Complex Effluent
Separation
Filtration
or
Centrifugation
or
Decantation
Effluent
Complex
Metal Recovery

Figure 3. Polyelectrolyte complex method.

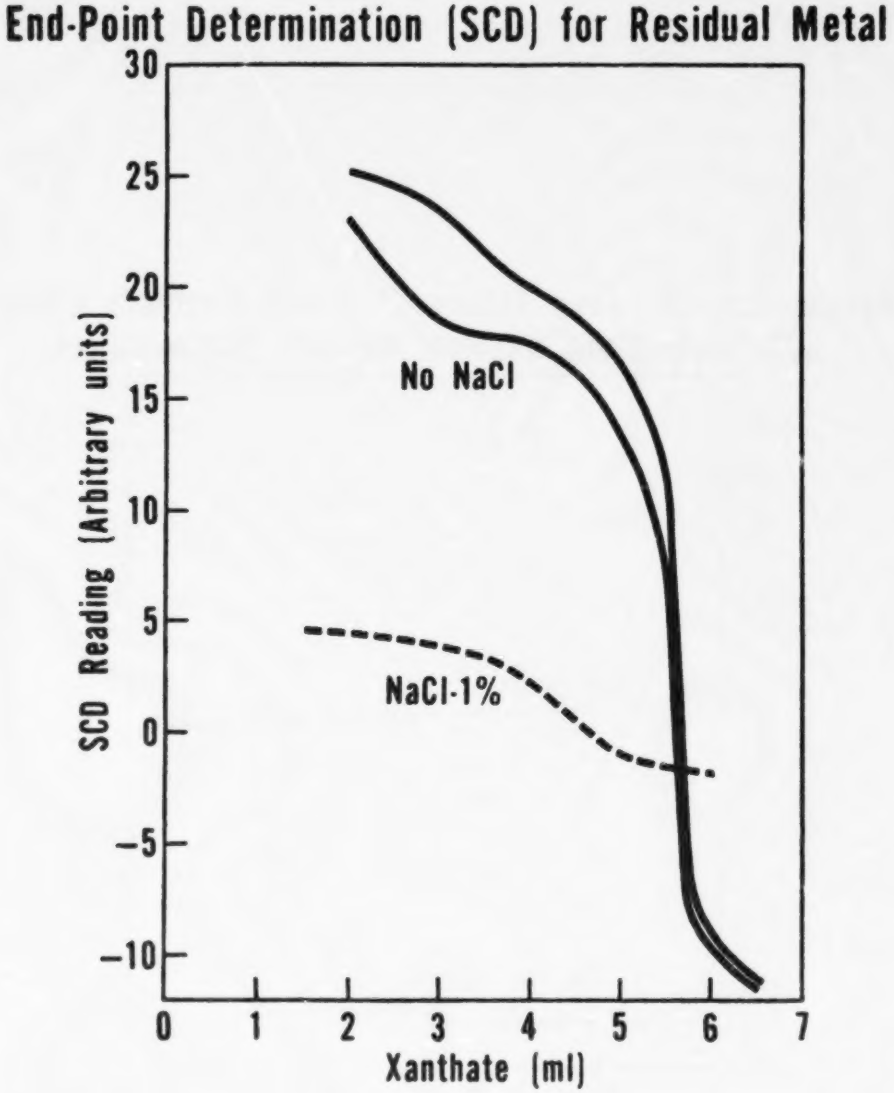


Figure 4. Typical streaming current detector (SCD) curves from titration of mercury(II) (5 mg) and poly(vinylbenzyltrimethylammonium chloride) (PVBTMAC) (10 mg) with starch xanthate [0.23 degree of substitution (DS), 1% (w/v)] in the presence (lower curve) and absence (upper curves) of sodium chloride [1% (w/v)].

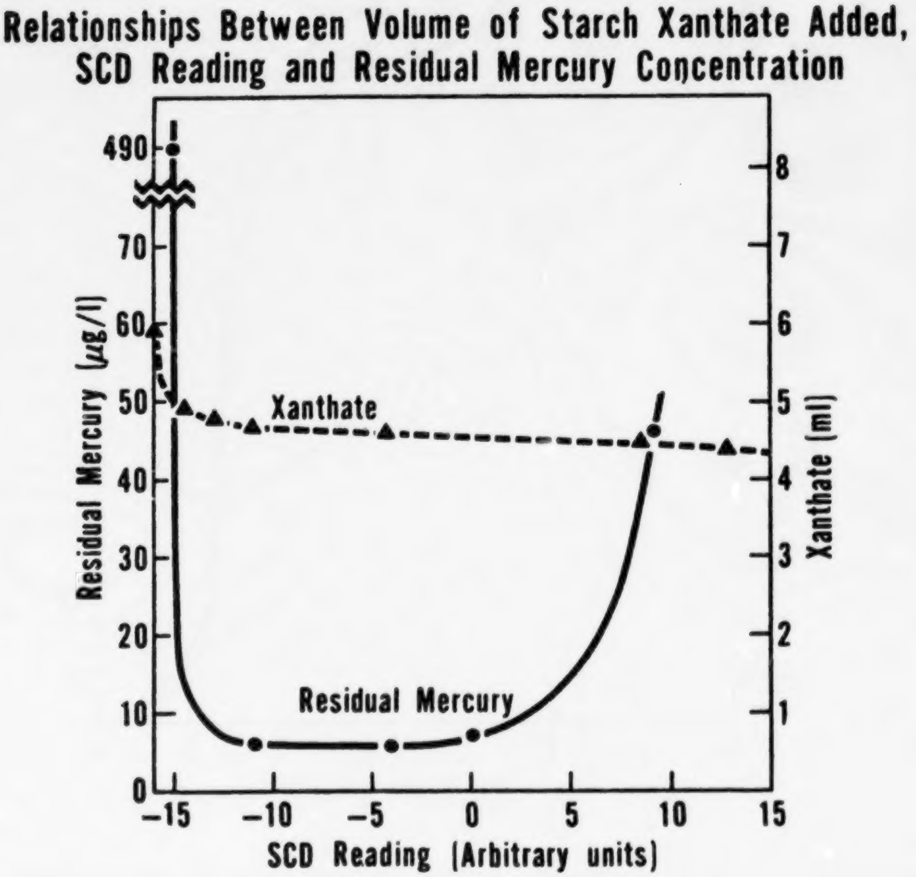


Figure 5. Relationships between volume of starch xanthate added, SCD reading, and residual mercury concentration. Fifty-milliliter samples containing mercury(II) (5 mg) and PVBTMAC (10 mg) were treated with starch xanthate [0.23 DS, 1% (w/v)].

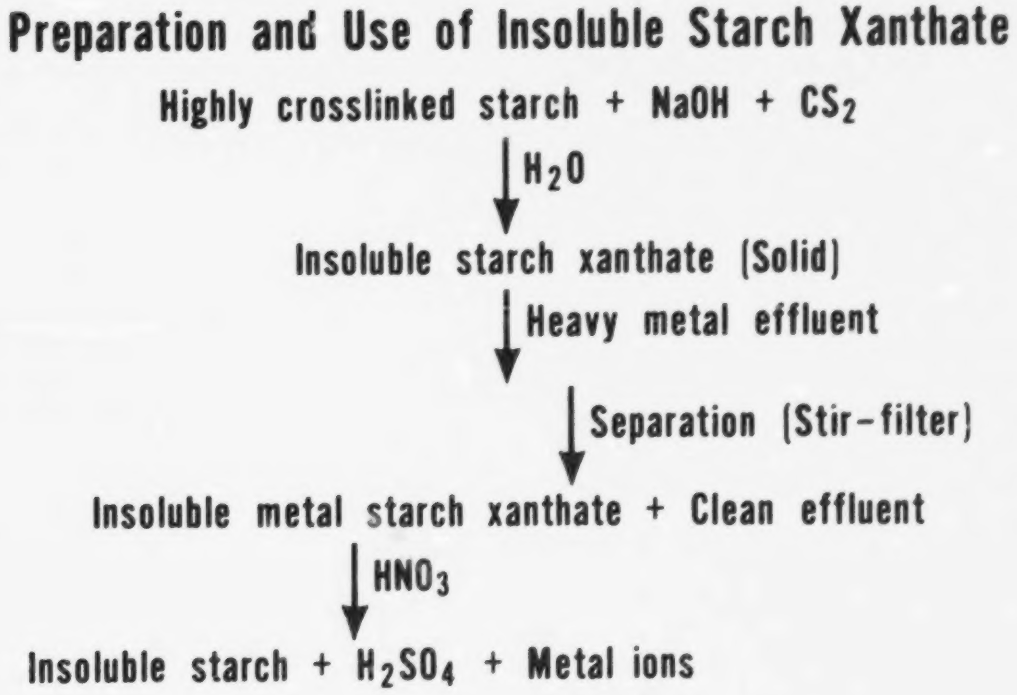

Preparation and Use of Insoluble Starch Xanthate
Highly crosslinked starch + NaOH + CS2
H2O
Insoluble starch xanthate (Solid)
Heavy metal effluent
Separation (Stir-filter)
Insoluble metal starch xanthate + Clean effluent
HNO3
Insoluble starch + H2SO4 + Metal ions

Figure 6. Insoluble starch xanthate method.

SUMMARY OF CONCLUDING REMARKS
PRESENTED AT THE SESSIONS
ON THE
REMOVAL PROCESSES OF
TRACES OF HEAVY METALS FROM WATER

C. Calmon
R. F. Probstein
C. J. King

C. Calmon

The symposium on "Traces of Heavy Metals in Water" has shown the economic and technical limitations in the removal processes. The symposium should be repeated in a few years to note if progress was made along the two parameters mentioned above. However, the speakers must take into consideration the following:

1. Potable water is delivered to a household after collection and treatment at a cost of about 50¢/1000 gallons, the volume being equivalent to 8000 pounds.

2. Tests must be run in accordance with standard water treatment procedures.

3. Solubility or loss of an absorbent or chemical additives can add high costs and may also prove to be toxic in itself.

It was quite evident from the data presented that there is no one favored method or one which is applicable to all ions or all concentration of ions present in the solution in question.

It is essential that each situation requires a total system approach which may include (1) process modification, (2) segregation of wastes, or (3) a combination of treatment methods.

Today, three processes appear to have merit because they are well established and their limitations and economics can be readily calculated; namely

1. evaporative processes where ionic concentrations are high.

2. ion exchange where ionic concentrations can reach to about 2000 ppm; and

3. chemical precipitation where the solubility product of the product formed is extremely low.

Evaporative processes have the disadvantage of high cost per unit volume of liquid treated but has the advantages of (1) not being affected by ionic concentration, (2) the final product is dry or in a concentration which can be reused, and (3) equipment and waste heat are frequently available.

Ion exchange has the advantage that the cost per unit volume of water treated is a function of the ionic concentration, the lower the concentration, the lower the costs. Aero ion exchange resins frequently have high selectivities for specific ions so that the resin can treat very large quantities of water per volume of exchange. However, the problem of regenerant waste in a solution strength of 5 to 15% can be a problem. Many inocuous ions present in the water may reduce the capacity of the resin as well as the purity of the recovered product and also some ions can foul the exchange leavages, with concentrations above permissible limits, may often appear during the operation.

Ion exchange today is applied successfully to many heavy metal wastes because the economics favor it, e.g., gold, geranium, chromium, copper and zinc recovery, the problem is how to get industries to use ion exchange to systems which show no profit in concentrating cheap ionic species. A solution to this problem would be the development of highly specific ion exchanges. This work should be carried out in a well-coordinated and planned program funded by EPA in place of the present method of solicited or unsolicited contract proposals for a specific ion. If zero discharge is ever to be attained economically, specific ion exchanges appear to be the most promising.

Chemical precipitation and coagulation must also be considered as these can be directed to the ion in question. If the solubility product is exceeded then the effluent from this treatment may be followed by a selective ion exchange resin.

Several new developments in polymeric resins should be watched, e.g., polymeric absorbents and macroporous resins capable of absorbing colloidal and complexed materials, thus making resins capable of removing trace heavy metal ions in solution or existing in colloidal or complexed forms.

R. F. Probstein

The most salient point to emerge from the papers on the use of thermal processes, reverse osmosis and electrodialysis for heavy metal removal is that insufficient effort has been devoted to the development of these methods for the specific purposes of heavy metals removal. Despite the fact that they could prove in many instances to be the only economic means of meeting upcoming EPA standards, they remain untried and undeveloped for a wide variety of situations. From the statements made at the Conference this would appear to stem in part from the equipment manufacturers' unwillingness on economic grounds to make the necessary R&D investments. It would seem appropriate, therefore, that until conditions change, EPA itself should assume the obligations for any R&D funding, with the public the recipient of both the developments and the cleaner water. The funds cited by Mason[1] as now being set aside by EPA for process technology development, pilot plant and demonstration testing would seem to fall far short of what is needed to meet the Agency's strict discharge and receiving water standards on the time scale envisaged.

Despite the fact that electrodialysis has been used commercially for well over a decade to separate out low molecular weight ionic species from brackish waters, no detailed examples were cited of its application to heavy metals removal. Prototype electrodialysis systems for treating electrodialysis systems have been discussed briefly in the literature (see, e.g., Ciancia[2]) but so far the process has been little studied over a wide range of conditions of heavy metal removal. However, its potential and advantages are obvious, particularly in that range of dissolved metal concentrations too high to make ion exchange economical and too low for optimum reverse osmosis performance.

Reverse osmosis has fared somewhat better in the attention it has received, as evidenced by the work reported by Houle[3]. Some bench scale studies on the rejection efficiencies for a variety of trace level heavy metal contaminants have also been recently reported by Mixon[4]. At this time, however, it is far from possible to characterize specifically reverse osmosis heavy metal rejection capabilities as a function of concentration, membrane types, system flow characteristics and fouling tendencies associated with the feed.

In my own paper[5] I pointed out that evaporation processes presently used for heavy metals separation suffer from their energy intensiveness. Vapor compression evaporation is the one method offering a distinct advantage in energy savings but it has had little testing on a variety of heavy metal distillates. Freezing, on the other hand, which appears to combine both energy savings and the advantages of limited corrosion is still in an embryonic stage, principally because of the limited funds available to mount a major development effort.

It has long been recognized that for the most part the problem of separating out metal impurities from water in the laboratory is not difficult, what is difficult is to carry out these separations economically and on a large scale. To do this requires process development not only in the laboratory and on bench scale but up through and including demonstration systems. From the papers presented at this Conference it would appear that many promising methods for heavy metals removal have not advanced beyond the laboratory stage because of insufficient funding and/or lack of incentive to move ahead.

References

1. Mason, R. W., "Overview on Heavy Metals Pollution Control at the Federal Level," (this Conference).
2. Ciancia, J., "New Waste Treatment Technology in the Metal Finishing Industry," Plating 60, 1037-1042 (1973).
3. Houle, P. C., "Reverse Osmosis" (discussant, this Conference).
4. Mixon, F. O., "The Removal of Toxic Metals from Water by Reverse Osmosis," Office of Saline Water R&D Progress Report No. 889, Sept. 1973.
5. Probstein, R. F., "Heavy Metals Removal by Thermal Processes," (this Conference).

C. J. King

It is apparent that the development of processes for metals removal is a separation problem of considerable challenge. The specifications which are put forward for desired purities are such that one often has to reduce concentrations by many orders of magnitude. As we have seen this is no easy task, nor should it be expected to be.

In view of the difficulties of economical metals removal, more attention should be devoted to the modification of the processes themselves which are sources of metal-bearing effluents. One would expect that process modification would often be less expensive than treatment of the original effluent.

It is apparent that there are today no "plug-in" proven processes. Because of this, a very considerable amount of research and development will be required if we are to deal effectively with the problem. This will require funding on a large scale and will require broad technical capabilities which are not now present in most of the companies who are confronted directly with the need for metals removal. It does not appear that a means of funding or coordinating this research presently exists, and it would therefore be a most appropriate government program.

With respect to the attractiveness of different processes which can be considered for metals removal, we have seen that there is no clear-cut forerunner. We have also seen that different processes become most competitive at different levels of metals concentration in the stream to be treated and for different effluent specifications. In addition to those processes discussed specifically at this Conference, electrochemical and liquid-ion-exchange processes deserve consideration for feeds of intermediate concentration ranges. Another important question is what should be the eventual destiny of the recovered metals. Often the amount involved is trivial in terms of economic worth. Recycle to an appropriate point in the main process will be the answer in some cases, but that will not be possible when the metallic species are not principal participants, products or side-products of the main process.

A COMPARATIVE OUTLINE OF CURRENT METHODS FOR THE ANALYSIS OF TRACE METALS IN NATURAL WATERS

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The mounting pressure for a cleaner environment has spawned explosive growth in the many aspects of environmental science. One of the many consequences of this enhanced scientific growth has been a demand for increasingly sensitive methods for the accurate monitoring of extremely low levels of environmental pollutants. This paper gives a brief preview of one particular aspect of the subject: a comparative outline of the current techniques available for the determination of trace levels of heavy metals in natural waters. Three general areas of methodology will be discussed and compared: 1) Atomic absorption spectroscopy, 2) Neutron activation, and 3) Polarographic methods. Preceding these discussions, some aspects of the crucial but little understood problem of sample preservation, storage, and transfer will be outlined.

SAMPLE PRESERVATION, STORAGE, AND TRANSFER

As the subsequent discussion will show, we are well into the era of routine analytical capability in the part-per-billion and sub-part-per-billion range for most aquatic contaminants, including most heavy metals. Such extreme sensitivity, however, has exposed a new and important problem which must be dealt with before any natural water sample can be reliably analyzed in the first place. The problem is simply that, when dealing with water characterizations in the part-per-billion and sub-part-per-billion range, previously negligible physical, chemical, and biological changes which occur in a natural water sample during storage and transfer now assume major significance. In many cases, unless special precautions are followed (e.g., proper chemical stabilization or choice of sampling and storage container material), there may be little or no resemblance between the sample taken and the sample analyzed. Obviously there can be no use for today's ultrasensitive analytical techniques if there is no equally precise capability in sampling storage and transfer. Unfortunately, progress in this important area has not kept up with the rapid development of increasingly sensitive analytical capability, and proper sample preservation is still largely a matter of trial-and-error. A few typical difficulties and suggested procedures are illustrative.

Adsorption of desired elements on sampler or transfer container walls may give significantly lower analyses; conversely, leeching of undesired contaminants from container walls may introduce false positive results or give significantly higher analyses if the element was already present in the sample. Scrupulous pre-washing of all containers is absolutely essential, and special washes with pure solutions of desired elements may also be required.

Although this paper is limited to a discussion of heavy metals, it is useful at this point to use information collected for phosphorus to illustrate the problem of adsorption and desorption, since it is one of the very few environmentally significant elements which have been systematically studied in this respect. Solutions containing <10-20 ppb phosphorus (typical for many lakes and streams) have been shown to undergo significant loss of orthophosphate while standing in Pyrex containers for 3-5 days (1), due to adsorption on the glass. This could only be eliminated by the use of polycarbonate containers which had been pre-washed with a solution of orthophosphate (1). In our laboratory, we have been able to store natural water samples for up to 4 days, but no longer, in 1-quart size PVC containers without significant drop in the phosphorus level.

Biological processes in natural water samples are also a major cause of significant changes in sample composition when working in the part-per-billion-and-less range. Addition of a stabilizer to kill or severely retard biological systems is necessary, provided the stabilizer itself does not introduce additional problems. The choice of stabilizer depends on many unfortunately not always known, sample parameters. The most common, effective means of stabilization is acidification to pH=2-3 with diluted nitric acid. Where a mercury or chloride anaylsis is not desired or conditions and methods don't otherwise preclude it, preservation with ∿4 ppm mercuric chloride is also very effective. Refrigeration, if used as a preservation technique where it is necessary that no chemical preservative of any sort be added, must be done very carefully so as to avoid freezing the sample, since this can cause the irreversible precipitation of many natural water components. The chief disadvantage with acidification as a preservation technique is that it can cause the desorption of contaminants from the container walls. Acid prewashing of containers can minimize this. Sometimes, the problems that arise with stabilizers are altogether unexpected; we found that acid stabilizing of water samples kept in PVC containers often caused slow leaching of the plasticizer from the container walls within

2-3 days. The plasticizer was an organic phosphate ester, and the error in the resulting phosphate analyses is obvious!

It should be re-emphasized that all of the above processes represent very small changes in an absolute sense, but such small changes become extremely significant when analyzing in the range of parts per billion and less. The only really reliable approach, then, is to analyze water samples immediately after they have been taken, or as soon as possible thereafter, preferably within the same day. Spiking control samples at the time of collection and ascertaining the degree of analytical "recovery" of the spike often serves to indicate the presence or absence of storage problems.

CRITERIA FOR THE SELECTION OF TRACE ANALYTICAL TECHNIQUES

Several methods are available today for the ultrasensitive analysis of heavy metals in natural waters. The most widely used are atomic absorption methods including both flame and the new flameless techniques, polarographic methods, including anodic stripping and pulse techniques, neutron activation, spark source mass spectrometry, and specific ion electrodes. The first two seem to enjoy the most widespread use, and are the subjects of the following brief discussions, although some comparisons have been made with neutron activation analysis. These techniques have been reviewed in depth elsewhere (2-4), and excellent bibliographies are available. Consequently, the present discussion assumes basic familiarity with the methods discussed and is limited to a practical comparison between the methods, particularly with respect to cost, sensitivity, ease of set-up and operation, and principal advantages and drawbacks.

The factors to be considered in selecting an analytical method for trace metal analysis may be listed as follows (2):

(a) the analytical operations should be reasonably simple in their execution;

(b) the hardware requirements should be met with relatively inexpensive intruments;

(c) sample manipulation and treatment should be minimal;

(d) simultaneous or rapid sequential multielement determinations should be possible;

(e) the power of detection of the technique should be in the low ppb and sub-ppb levels;

(f) the technique should be highly selective (relatively free from interferences).

In general, the typical environmental analytical laboratory will be handling a large number of parameters for a large number of water samples routinely, and usually with non-professional operators. Consequently, speed, simplicity, and reliability with minimum special effort are indispensable. Pre-concentration of the sample to be able to operate in the sub-ppb range is usually no longer necessary with some of the refined methods now available, as seen below.

ADVANTAGE/DISADVANTAGE COMPARISON

Table I compares the chief advantages and disadvantages of the two techniques for atomic absorption spectroscopy for neutron activatio analysis, and for polarographic methods.

TABLE I

Method	Advantages	Disadvantages
Atomic Absorption Flame	fast; good precision; inexpensive	can't do many elements simultaneously
Flameless	can achieve several orders of magnitude sensitivity increase over flame methods	limited to single element analysis; not as fast as flame methods
Neutron Activation	high sensitivity and precision; does many elements simultaneously; can analyze refractory materials, such as ceramics	usually the most expensive method, but seldom most sensitive
Polarographic	high sensitivity and precision; does several elements simultaneously; very inexpensive	can become very tedious operation settling up for trace analysis; may be subject to complications due to unwanted solution equilibria, e.g. conplexation.

The additional cost-range comparisons given in Table II show at once that neutron activation analysis, with its extremely high equipment cost, cannot be considered truly competitive as a trace analytical technique for routine use with natural water samples.

TABLE II

COST COMPARISON OF INSTRUMENTATION

Equipment	Range of Cost
Atomic Absorption Spectrophotometer (Flame)	\$4,000 to \$15,000
Atomic Absorption Spectrophotometer (adaptable for flameless)	\$9,000 to \$20,000
Neutron Activation Analyzer	over \$100,000
Polarographic Analyzer	\$2,000 to \$3,000

Its real utility is in its applicability to the analysis of intractible or refractory materials such as ceramics, rocks, etc., since a solid sample can be readily bombarded with neutrons and counted.

Other points in Table I warrant further, brief discussion. While it is felt that, in general, spectroscopic techniques require somewhat less skilled technical personnel and involves considerably less set-up than electrochemical (polarographic) methods. (2-4), this is offset by the fact that equipment costs for the electrochemical methods are significantly lower than for atomic absorption spectroscopy, while sensitivities and detection limits are quite comparable, as is shown in Table III. More importantly, however, atomic absorpti spectroscopy has still not been demonstrated to be conveniently and practically adaptable to the routine, simultaneous analysis of severa elements in a given sample, and the hollow cathode lamp must be changed over for each new element. Instrumentation for simultaneous multi-element analysis by atomic absorption spectroscopy is not yet available (3a). In contrast, polarographic methods are by nature perfectly suited to the rapid, simultaneous determination of several trace metals in a given water sample.

Finally, all methods for trace metal analysis are affected to varying degrees by so-called "matrix" effects: the effect of the surrounding sample environment both liquid and gaseous, upon the interaction between the desired element and the detection system. Means for minimizing matrix effects are discussed in detail elsewhere (2,5), but one particular solution effect which could seriously affect trace metal determinations by polarographic techniques warrants specific discussion here. The potential at which a given metal oxidation/reduction will occur is, of course, affected by any solution equilibria in which the metal is involved in the water sample.

Many natural waters today may contain any of several chelating agents, such as NTA (nitrilotriacetic acid), which will shift the redox potential of a metal ion through complexation. Thus, the position of a complexed metal wave or peak in a polarogram could easily be mistaken for this or another, uncomplexed metal. In fact complexed and uncomplexed trace metals were distinguished and determined in secondary sewage effluent by an anodic stripping polarographic technique (5).

DETECTION LIMITS

Table III compares the detection limits for atomic absorption, neutron activation, and polarographic techniques. For the elements listed, neutron activation analysis gives no improvement in sensitivity over the other methods, and in most cases is considerably less sensitive, precluding its routine application to aquatic

TABLE III

DETECTION LIMITS, PARTS PER BILLION

Element	Atomic Absorption			Neutron Activation	Polarographic
	Flame		Flameless		
Ag	3^{a}	10^{b}	0.04^{d}	2	0.1
As	250	50	20	5	20
Cd	0.6	1	0.02	200	5(.2)^{e}
Cu	3	5	1.4	4	5(.2)^{e}
Fe	5	4	0.6	50,000	100
Hg	200		20, 1^{c}	5	
Mn	3	5	0.1	0.1	100
Pb	20	10	1.0	40,000	5(.5)^{e}
Se	480		20	400	.10
Sn	30		12	10,000	5
Zn	2	5	0.016	400	5(1)^{e}

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[a] Detection Limits reported by Varian Techtron.

[b] Detection Limits reported by EPA using Instrumentation Laboratories Model IL-153 instrument. Cf. "Methods for Chemical Analysis of Water and Wastes, 1971, U.S. Environmental Protection Agency.

[c] Detection Limit for Hg using chemical digestion/reduction techniques
[d] Detection Limits reported by Varian Techtron for carbon rod atomizer
[e] Anodic stripping techniques; e.g. DPAS.

trace metal analysis. Atomic absorption and polarographic methods exhibit very comparable, frequently very low, detection limits.

Recent advances in both spectroscopic and electrochemical methods have extended detection limits for most heavy metals to truly low levels, in many cases under one ppb. Among such techniques are the flameless variant of atomic absorption (2,3a)[*], and differential pulse anodic stripping polarography (DPAS) (4b).[†] Table III shows that each of these methods is capable of extending the detection limit downward by up to an order of magnitude or more compared to standard flame atomic absorption methods on the one hand and direct conventional or direct pulse polarography on the other. Essentially, both these variants have extended the detection limits of their respective methods into the sub-ppb range for many heavy metals while at the same time eliminating pre-concentration as a necessary preliminary step.*† Of course, it must be remembered that such ultra-sensitivity entails some additional cost, additional operator skill, and much additional attention to the problems of sample storage and transfer.

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[*] In flameless atomic absorption procedures, the sample is injected into or onto a small electrically heated furnace or filament rather than aspirated into a flame to effect atomization. Consequently, the entire sample is atomized directly into the light path. Since the furnace or filament is heated in stages to evaporate solvent, ash organic matter and then atomize the element,several injections can be made into or onto the furnace or filament and solvent removed prior to the atomization stage, in effect carrying out a rapid, convenient concentration step right in the apparatus.

[†] Anodic stripping polarography differs from direct polarography in that in the former method, a trace metal is first plated out onto a mercury electrode (hanging drop), and is then re-oxidized into solution. Current/potential curves are measured during the oxidation stage and the element determined using calibration curves. Dilute samples can be analyzed because the desired element is first "pre-concentrated" in the mercury drop. Differential pulse anodic stripping (DPAS) polarography is a refinement which further increases sensitivity by minimizing capacitance charging currents. This is achieved by applying a pulse technique in the re-oxidation stage. Cf. ref. 4b.

Finally, analysis for mercury should be discussed separately both because of its increasing ecological significance in the public eye and because it cannot be handled well by any of the methods discussed here. Table III shows the relative insensitivity of conventional flame atomic absorption analysis of mercury, due to its volatility. It cannot, of course, be determined polarographically since these methods employ mercury cathodes. Instead, satisfactory sensitivity for mercury is achieved by so-called "cold-vapor" atomization techniques, whereby the sample is first oxidatively digested (usually with permanganate/sulfuric acid) to convert all mercury compounds to inorganic salts, and the mercury is then vaporized monatomically into a gas cell in the radiation path by means of chemical reduction (usually with stannous chloride). Table III shows that the detection limit for mercury is improved at least tenfold over conventional flame atomic absorption procedures by the use of such "cold-vapor" chemical atomization techniques. One of the many types of apparatus for "cold-vapor" mercury detection is shown on Figure 1 (6).

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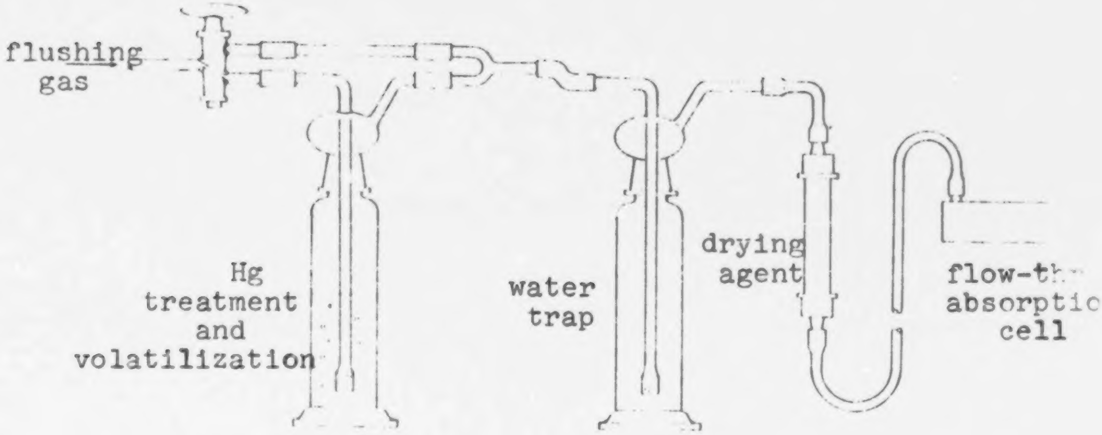
FIGURE 1


flushing gas
Hg treatment and volatilization
water trap
drying agent
flow-th
absorptio
cell

Apparatus for "cold-vapor" (flameless) atomic absorption determination of mercury

ACKNOWLEDGEMENT

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THE USE OF ATOMIC ABSORPTION SPECTROSCOPY IN ANALYZING FOR TRACE METALS IN THE ENVIRONMENT

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During the last ten years a revolution has been occurring in the field of trace metal analysis. That revolution has been the advent of atomic absorption spectroscopy. Ten years ago chemists were spending large amounts of time in analyzing for trace metal by colorimetric methods . The addition of many chemical reagents and the use of tedious extraction techniques were usually necessary to measure low levels of metallic constituents in samples brought to them. Quite often the results from these colorimetric and wet chemical analyses had to be taken with a grain of salt because of the many interferences in such methods. Atomic absorption spectroscopy has changed all that and has provided the modern day analyst with a rapid, sensitive, specific, and highly reliable method of analyzing for trace metals in the environment just at the time that such a method is direly needed. The atomic absorption technique of metals analysis is not only widely accepted but is generally the preferred method of metals analysis in education, government and industry and has been endorsed by the American Society for Testing and Materials(1) and the Environmental Protection Agency(2).

Instrumental Principle

Atomic absorption is based on the fact that metal atoms, reduced to their "ground" state, will absorb light of the same wavelength that would normally be emitted by the same metal atoms when in an excited state. Schematic diagrams of the two different types of atomic absorption spectrophotometers available on the market are shown in Figures 1 and 2. A beam of light, characteristic of the element to be analyzed, is modulated by a chopper and then passed through a flame or other device designed to provide sufficient thermal energy to dissociate the metal atoms in the sample from their various compounds and reduce them to the ground state. The ground state atoms then absorb the modulated light from the source. The amount of light absorbed is a measure of the concentration of the element of interest in the solution being analyzed. Using this principle, as many as 70 different elements can be analyzed.

Advantages of Atomic Absorption

There are numerous advantages to the environmentalist in using atomic absorption for detecting low levels of metallic elements. First of all, atomic absorption is a highly specific method of analysis. In colorimetric techniques it is usually very difficult, if not impossible, to find a reagent which is specific to a certain metal to the exclusion of all others. Consequently, numerous other metals usually interfere. Also, flame emission analysis is subject to numerous spectral interferences which cause spuriously high results when certain interfering metals are present. None of these problems are encountered in atomic absorption. Spectral interferences are virtually non-existent in atomic absorption and the method is highly specific for each metal analyzed.

Another advantage which atomic absorption offers is that it is relatively free from chemical interferences. Such interferences do exist but they are relatively few in number and, when they do occur, can usually be obviated with relative ease.

Another important factor in the rapid acceptance of atomic absorption is that it is fast and economical. Today, many analyses which used to take hours to perform can be done by atomic absorption in a matter of seconds. In addition, the cost of equipping a laboratory to perform atomic absorption analysis is moderate. Most commercially available instruments cost somewhere in the neighborhood of $10,000 and some single beam instruments can be obtained for as little as $5000. In a laboratory which performs many metals analyses, an atomic absorption spectrophotometer will easily pay for itself in a short period of time.

Finally, probably the biggest advantage which atomic absorption offers the environmentalist is its high sensitivity for most elements. In our laboratories, we calculated the detection limits for 24 different elements using a Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer. (The detection limit is defined as the concentration of an element in water solution which gives a signal twice the size of the peak-to-peak variability of the background.) These detection limits are listed in the attached table. Note that a majority of the detection limits are in the low ppb range while the detectability for three of the elements (calcium, magnesium and beryllium) is less than one ppb. While these detection limits cannot always be attained when analyzing real samples, they give some indication as to the applicability of atomic absorption to trace metal analysis.

In addition to the high sensitivity attainable by direct aspiration of a sample into the flame, numerous methods have been devised for increasing the sensitivity of atomic absorption. Chelation of the metal ions in solution and extraction of the resultant complex into an organic solvent can increase the sensitivity of atomic absorption by one or two orders of magnitude(3).

Other methods of increasing the sensitivity of atomic absorption measurements have been introduced in recent years. The most successful of these have been the tantalum boat(4) and Delves cup(5) technique. These methods are based on the fact that some metals are sufficiently volatile to be vaporized at the temperature of the air-acetylene flame and involve direct introduction of the sample (after drying) into the flame on a tantalum strip or nickel cup. This technique, however, is limited to only those metals which will vaporize at or near 2000°C. The only metals of concern to environmentalists which fit into this category are lead, cadmium, zinc, silver, arsenic and selenium.

Flameless Techniques

Enormous strides have been made in recent years in improving the sensitivity of atomic absorption measurements by using electrically heated graphite tubes or similar devices for atomization of samples(6). These flameless atomization devices provide great increases in sensitivity resulting in detection limits two or three orders of magnitude below those achieved with most flame techniques because all of the sample is atomized (compared with only 5-10% when flame methods are used) and the residence time of the ground state atoms in the light beam from the source is greatly increased. In addition to increased sensitivity, only a very small amount of sample is required using these devices and the flameless methods can be used for analysis of all but the most refractory metals.

Another flameless technique which has been extensively used by environmentalists for the last five years is the "cold vapor" atomic absorption analysis of mercury(7). This type of analysis is different from most atomic absorption methods in that chemical reagents rather than thermal energy are used to reduce the mercury to the elemental ground state. In the method, mercuric ions in solution are reduced to elemental mercury by the action of stannous ion. The mercury vapor is then pumped into a quartz absorption cell positioned in the light path of an atomic absorption spectrophotometer. The amount of light absorbed at the resonance wavelength of mercury is a measure of the concentration of mercuric ion in solution. Using this technique, mercuric ion can be measured down to concentrations of a fraction of a ppb.

Applications

Atomic absorption has found many different applications in the field of environmental analysis. The most immediate and obvious application is to the analysis of water. This includes natural waters, saline waters and industrial wastewater(8,9,10). The most extensive application of atomic absorption to the analysis of natural waters has been the analysis of mercury(7,11). The concern in recent years over contamination of the environment with mercury as a byproduct of various industrial processes resulted in an urgent need for analysis of natural waters for mercury content. The cold vapor atomic absorption method of analyzing for mercury provided the sensitivity and reliability needed to meet the crisis. Almost every metal of environmental concern found in natural waters can and is routinely analyzed by atomic absorption methods in laboratories throughout the nation. This includes seawater as well as freshwater.

Another important application of atomic absorption methods is to the analysis of industrial wastewaters(10). As is well known, the main source of pollution in our lakes and streams is the effluent from industrial processes. In order for industry to monitor the quality of a wastewater being dumped into a waterway and for government to enforce quality standards an accurate means of analyzing wastes is required. The specificity and freedom from interference of atomic absorption permits this technique to play a major role in regulating the quality of industrial waste effluents.

Many times pollutants are lodged in the sediments found at the bottom of lakes and streams. Atomic absorption has also been applied to this type of material(12). In most cases where metal analyses are desired, the metals are leached from the sediment with acids and determined by atomic absorption.

Even various marine organisms have yielded to the versatile analytical technique of atomic absorption. Methods of analyzing for mercury in fish by atomic absorption are well established(13) and the analysis of cadmium in marine organisms by this technique has been reported(14). In most cases these analyses are performed by homogenizing the flesh of the organism and chemically oxidizing the organic material by means of acid reflux. The resulting solution is then analyzed for mercury using the cold vapor method and for other metals either by direct aspiration or flameless methods.

Some of the pollutants in the atmosphere end up being precipitated in rain or snow. Flameless atomic absorption techniques have proved their worth in analyzing for these trace contaminants(15).

Atomic absorption has been used to monitor air pollution as well as water pollution(16). In analyzing the metal content of particulate matter in the air, the air is usually drawn through a filter. The filter is then either burned or washed with acid solution. The particulate matter that had been trapped is then solubilized and analyzed by atomic absorption. This technique has been found very successful in monitoring the amount of lead in airborne particles(17).

Another place where lead in the environment has created a problem is in household paints. Lead poisoning in young children who have chewed on the walls and woodwork of old houses that have been painted with lead-based paint is fairly common(18). As a result, the federal government has laid down stringent regulations governing the amount of lead permitted in household coatings(19,20). Atomic absorption is the only method that provides sufficient sensitivity to meet the analytical requirements of these regulations. In analyzing for lead in paint, either the paint is ashed and the residue dissolved in acid solution(21) or else the Delves cup method is used whereby the paint is suspended in an appropriate solvent and a portion of the slurry is transferred to a nickel cup. After drying, the cup is inserted into the air-acetylene flame where the lead is volatilized and measured by atomic absorption(22).

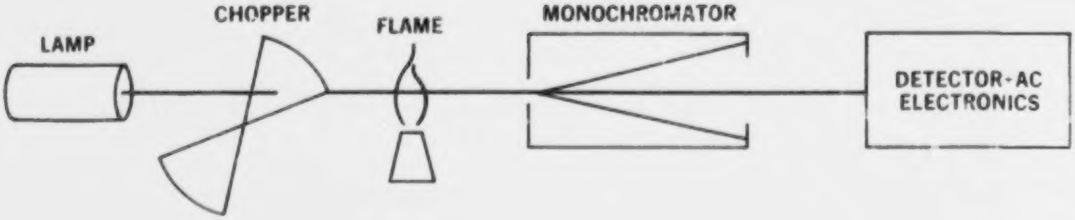
Similar methods are used in the field of biochemistry in diagnosing and treating victims of environmental pollution. The Delves cup method has been used quite extensively in clinical laboratories for the last few years to determine lead in blood(5). The new flameless techniques have also begun to be used in clinical applications for determining concentrations of toxic metals due to the high sensitivity attainable and small sample size requirements of these methods(23).

Besides the many direct applications of atomic absorption to environmental problems there are many indirect applications as well. The use of atomic absorption as a quality control tool in the food industry is one such application(24). The analysis of coal, oil, rubber and plastics provides a means for evaluating the amount of toxic metal contaminants introduced to the environme by these common substances.

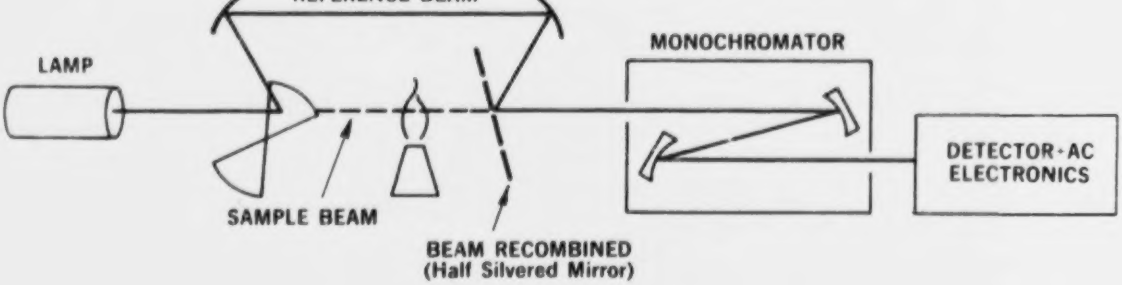
In light of the fact that atomic absorption methods are continuing to grow in scope and application there is no doubt that this analytical technique will continue to play a large role in monitoring the level of contaminants in our environment and in pollution abatement.

Detection Limits for Various Metals by Atomic Absorption With the Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer

Element	Detection Limit, mg/l
Aluminum	0.04
Antimony	0.06
Arsenic	0.6
Barium	0.06
Beryllium	0.0009
Boron	2.6
Cadmium	0.002
Calcium	0.0004
Chromium	0.007
Cobalt	0.016
Copper	0.003
Iron	0.003
Lead	0.025
Magnesium	0.0003
Manganese	0.003
Molybdenum	0.014
Nickel	0.006
Selenium	0.6
Silicon	0.08
Silver	0.002
Tin	0.12
Titanium	0.06
Vanadium	0.002
Zinc	0.002


CHOPPER
FLAME
MONOCHROMATOR
LAMP
DETECTOR-AC ELECTRONICS

SINGLE BEAM AC SYSTEM OF ATOMIC ABSORPTION
FIGURE 1


REFERENCE BEAM
MONOCHROMATOR
LAMP
DETECTOR-AC ELECTRONICS
SAMPLE BEAM
BEAM RECOMBINED
(Half Silvered Mirror)

DOUBLE BEAM AC SYSTEM OF ATOMIC ABSORPTION
FIGURE 2

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THE OCCURRENCE OF TRACE METALS IN SURFACE WATERS

Robert C. Kroner

The spectrographic measurement of trace metals in surface waters of the United States was performed routinely by the Water Pollution Surveillance System of the USPHS from the years 1960 to about 1968. The system, which is no longer operated, was established in 1957, in cooperation with industry, state, and local authorities and other Federal agencies with related responsibilities for the collection and dessimination of basic data on water quality. The Surveillance System at its peak consisted of about 130 sampling points located on major waterways throughout the United States. Local personnel at the sampling sites collected and mailed samples to Cincinnati where they were analyzed. In addition to trace metals, data was also collected for physical, chemical, biologic, microbiologic and radiologic parameters.

The information and statistical observations given in this paper are taken from the analysis of approximately 1500 samples collected over a five-year period. The analyses were performed on a direct reading emission spectrograph using a rotating disc according to the method described by Kopp and Kroner.(1)

TRACE ELEMENTS

The source and significance of dissolved minerals are very important in evaluating water quality. Indeed, the spectrographic analysis of water commonly reveals the presence of a surprisingly large number of elements, most in only trace amounts.

The significance of minor elements in human metabolism is not understood completely, but much progress has been made by biochemists, physicians, and public health scientists. For instance, cobalt, copper, zinc and certain other metals are believed to be important catalysts in the biosynthesis of amino acids, whereas certain forms of arsenic, lead and cadmium are known to be significantly toxic.

The 1968 Water Quality Criteria(2) report discusses the significance of a number of trace metals and attempts to set limiting standards as they affect public water supplies, aquatic life, agricultural uses and industry. Table 1 shows the criteria for trace elements in drinking water supplies.

With regard to agriculture, variations and interactions of soils, plants, water and climate preclude the establishment of a single set of criteria to evaluate all water quality characteristics. Toxic limits for trace elements which would be generally applicable to all soils and all crops are not easily defined. In general, trace element tolerances for irrigation waters are much higher than for other farmstead uses.

Industrial uses present much the same problem, inasmuch as water that meets the standard for the textile industry may not be acceptable to the food canning industry, and so on. However, industrial requirements are not nearly as stringent as those for public water supplies. In the majority of instances, a water that meets the criteria for public water supplies, as shown in Table 1, will also be acceptable for fish and aquatic life, livestock and other agricultural uses as well as for industrial uses. In general, the criteria for public water supplies are much the same as those given in the 1962 revised USPHS Drinking Water Standards.(3)

Among the listed materials that fall into the trace metal category and that may be measured spectrographically are arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese

(Mn), silver (Ag), and zinc (Zn). Other trace metals also occur with varying frequencies in river waters and may be of significance, even though their roles in physiologic processes are not completely understood. For this reason, in addition to those already listed, boron (B), molybdenum (Mo), aluminum (Al), beryllium (Be), nickel (Ni), cobalt (Co), vanadium (V) and strontium (Sr) were also routinely monitored.

The aforementioned trace elements, along with many others, originate from a variety of sources, but can be classified into three principal groups:

1. Elements contributed by soluble materials chemically weathered from soil and rocks.
2. Elements that are concentrated selectively by vegetation and find their way to surface waters after decay and runoff.
3. Industrial sources, especially those devoted to mining, alloying, and cleaning and plating of metals.

Although the first two sources tend to provide normal or expected trace-element levels, it is with the last source that our main interest lies.

Figure 1 shows the percent frequency of detection for trace elements in waters of the United States as determined from the analysis of over 1500 surveillance system samples. Barium, boron, and strontium are found in measurable concentrations in all samples; iron, zinc, copper, and manganese occur between 60 and 80 percent of the time; and aluminum, molybdenum, chromium, and lead, between 20 and 30 percent. Beryllium, vanadium, cadmium, and cobalt, however, are rarely found, and their presence would indicate an unusual source of pollution. From experience, it is possible in many instances to predict beforehand what will be found in a particular stream. Trace-element levels in some streams remain remarkably consistent; others fluctuate considerably.

Figure 1 shows only the frequency of detection of the nineteen elements included in the analytical program. The mean concentrations and ranges of concentrations of the metals are shown in Table II. Elements such as zinc, boron, iron, molybdenum, manganese, aluminum and strontium are observed occasionally at concentrations exceeding 1 mg/liter. Other elements, including cadmium, arsenic, copper, nickel, cobalt, lead, chromium and barium, are observed with lesser frequency and at approximating one tenth the concentrations found for the former group. Beryllium and silver, two metals that are rarely seen, occur at concentrations generally below 1 μg/liter.

An example of trace metal concentrations in spectrographically "clean" and "dirty" streams is shown in Table 3.

The St. Marys River is a stream that carries a heavy traffic of shipping but little or no industrial discharges. The Cuyahoga River receives numerous industrial discharges especially from the metals industries as it flows through the city of Cleveland. By comparison, the concentrations in the Cuyahoga River are many times higher for most metals. Zinc, boron, manganese, aluminum, lead, chromium and nickel are increased by large factors. In industrial streams such as the Cuyahoga, these metals slowly precipitate onto the stream bottoms, where they serve as a constant source of metals for re-solution into the flowing supernatants. Further, if dredging of the stream is required, the bottom sediments are extremely high in trace metals and disposal of the sediment creates another problem.

When the Surveillance System initiated the routine measurement of these trace elements, it was concerned primarily with elements in solution because any suspended material would be removed before it reached the consumer. While the philosophy of this approach is valid, it does not measure the total trace element load in the stream. It should be emphasized at this point, and strongly so, that not enough is known about the trace elements associated with river-borne suspended matter. Water quality criteria selected for trace elements in solution ignore or overlook the possibility of trace metals in the sediment load. Current laboratory practices are to analyze both the dissolved, as well as the suspended, fraction.

When natural water samples are filtered through a micropore filter and the suspended and dissolved fractions analyzed separately, the data obtained shows, in a general way, the solubilities of the metal salts. A review of the data indicates that some metals occur much more frequently in the suspended matters than in solution. This is particularly true of iron, aluminum, manganese, nickel and lead. Conversely, strontium, boron, copper and cobalt are more likely to be found in solution. Tables 4 and 5 show the relationship between metals in solution and metals in suspension. An analytical difficulty arises when one needs to discriminate between naturally-occurring and industrially-sourced metals in suspension. Types of clay consist of aluminum and iron, and dissolved metals can and do, adsorb onto the clay particles. An additional analytical burden is placed upon the analyst when it is necessary to distinguish between the sources of metals in natural waters.

SUMMARY

This paper has reviewed sources and concentrations of trace metals in surface waters of the United States. The mean concentrations of metals in natural waters have been discussed and the difference between a spectrographically "clean" and "dirty" stream is shown.

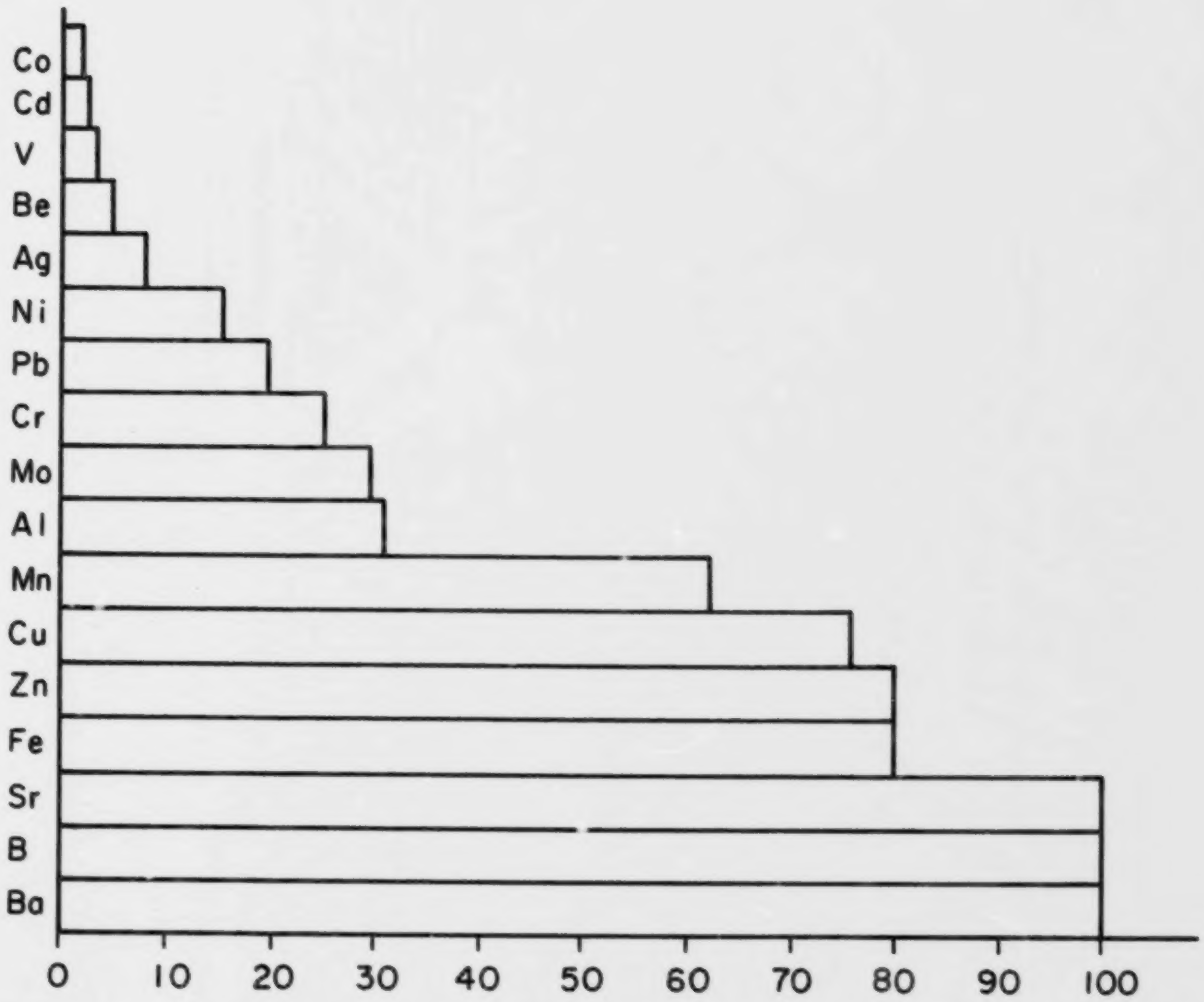

Figure 1.- Frequency of detection for trace elements in waters of the United States. (1500 samples)

TABLE 1

SURFACE WATER CRITERIA FOR TRACE ELEMENTS IN PUBLIC WATER SUPPLIES

Metal	Permissible Criteria, mg/l	Desirable Criteria, mg/l
Arsenic	0.05	Absent
Barium	1.0	"
Boron	1.0	"
Cadmium	0.01	"
Chromium^{+6}	0.05	"
Copper	1.0	Virtually Absent
Iron (filterable)	0.3	" "
Lead	0.05	Absent
Manganese (filterable)	0.05	"
Selenium	0.01	"
Silver	0.05	"
Zinc	5	Virtually Absent

Absent - The most sensitive analytical procedure in Standard Methods (or other approved procedures) does not show the presence of the subject constituent.

Virtually Absent - This terminology implies that the substance is present in very low concentrations and is used where the substance is not objectionable in these barely detectable concentrations.

TABLE 2

SUMMARY OF TRACE ELEMENTS IN WATERS OF THE UNITED STATES*

Element	Frequency Of Detection, %	Observed Positive Values, µg/l Max.	Observed Positive Values, µg/l Mean
Zinc	76.5	1183	64
Cadmium	2.5	120	9.5
Arsenic	5.5	336	64
Boron	98.0	5000	101
Phosphorus	47.4	5040	120
Iron	75.6	4600	52
Molybdenum	32.7	1500	68
Manganese	51.4	3230	58
Aluminum	31.2	2760	74
Beryllium	5.4	1	0.19
Copper	74.4	280	15
Silver	6.6	38	2.6
Nickel	16.2	130	19
Cobalt	2.8	48	17
Lead	19.3	140	23
Chromium	24.5	112	9.7
Vanadium	3.4	300	40
Barium	99.4	340	43
Strontium	99.6	5000	217

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*Based on 1500 samples.

TABLE 3

COMPARISON OF TRACE METAL CONCENTRATIONS IN POLLUTED AND UNPOLLUTED RIVERS*

	Cuyahoga River (Cleveland)		St. Marys River (Sault Ste. Marie)	
Metal	Freq. %	X, µg/l	Freq. %	X, µg/l
Zn	100	423	100	46
B	100	302	100	10
Fe	69	59	80	24
Mn	88	285	60	2
Al	19	27	71	6
Cu	31	9	100	6
Ba	100	50	100	11
Sr	100	148	100	15
Pb	12	28	53	5
Cr	19	11	20	3
Ni	69	70	20	11
Mo	12	27	33	9
Cd	19	64	0	0

TABLE 4

Mean Concentration and Percent Occurrence of Trace Elements*

	DISSOLVED			SUSPENDED		
Element	Range of Positive Values, µg/1	Percent Occurrence	Mean µg/1	Range of Positive Values, µg/1	Percent Occurrence	Mean, µg/1
Strontium	4-520	100	104	2-3	17	2
Boron	2-750	100	72	3-108	86	16
Barium	5-195	100	43	1-65	97	11
Zinc	6-97	91	63	5-151	90	30
Copper	3-280	80	24	3-66	85	10
Aluminum	1-1,875	25	85	3-1,440	87	316
Manganese	1-3,230	56	330	2-442	98	100
Iron	2-144	70	19	7->2500	100	>395

*At seven selected stations.

TABLE 5

Concentration Ranges and Percent Occurrence for Some Lesser Elements*

Element	DISSOLVED		SUSPENDED	
	Range of Positive Values, µg/l	Percent Occurrence	Range of Positive Values, µg/l	Percent Occurrence
Vanadium	15-54	3	12, 13	2
Cadmium	3-11	4	6, 16, 35	3
Silver	0.7-3.0	4	0.5-2.5	5
Cobalt	13-48	12	8-13	8
Chromium	2-25	23	3-13	38
Beryllium	0.03-3.2	30	0.04-2.35	39
Nickel	3-86	35	5-900	20
Lead	6-205	25	10-625	35

*At seven selected stations.

ION SELECTIVE ELECTRODE MONITORING FOR TRACES OF HEAVY METALS

by

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Ion-selective electrodes can be most readily used to monitor relative changes in concentration of traces of heavy metals in a variety of aqueous solutions. Note the emphasis on changes in concentrations. Absolute concentrations may be determined only after very careful electrode calibrations. If very accurate analytical results are required, samples must still be taken to the laboratory for careful work with either ion-selective electrodes or other, more precise analytical techniques. Automated monitoring with ion-selective electrodes will not replace the analyst, but can relieve him of much of the monotony of analyzing routine samples that are usually within specifications. The ion-selective electrode signals any significant deviation from a preset condition, allowing the operator to take a sample and the analyst to determine very carefully the exact concentration of the particular ionic species involved. An added advantage of ion-selective electrode monitoring of process streams is that it can also signal the operator or the control computer that a change or an upset has occurred in the process so that the various non-continuous monitors can be integrated and appropriate actions taken.

It may be convenient to think of a three-light system in connection with continuous automated monitoring with ion-selective electrodes. If the concentration of the species to be monitored is at its designed level and well within the prescribed limits, then the light as controlled by the electrode is green and there is no need to sample the stream. If significant changes in concentration occur (>25%), the light changes to amber, signaling the operator to check the process and take samples for laboratory analyses. If the concentration continues to change and reaches a level where there is significant probability that the process is grossly out of specification and that damage to personnel, equipment, or the environment can occur, then a red light is turned on, alarms are sounded, and the process may be automatically shut down.

With such a three-light system samples are taken for laboratory analysis only when the ion-selective electrodes indicate there has been a deviation from the normally specified process concentrations. In addition, signals from the ion-selective electrodes can be used to adjust other operating parameters such as flows, temperature, and concentration of reactants.

Ion-selective electrodes have been applied to monitoring heavy metal ions in saline and brackish waters (1,2). Applications of these electrodes to several non-heavy metal ionic species have been described by Light (3) and Jasinski and Trachtenberg (4). Orion Research Incorporated, Cambridge, Mass., has published several booklets that list a large number of commercially available electrodes, how they operate, interferences, limits of detection, and an extensive bibliography. These are available from Orion's Technical Service Department (5).

Ion-selective electrodes in combination with a suitable reference electrode yield a potential response which is Nernstian with respect to the selected ion. The potential developed between the ion-selective electrode and the references is proportional to the logarithm of the concentration of the selected ion (C_s), provided the ionic strength of the solution does not change (constant activity coefficient). Equation (1) describes this relation:

$$E = E_o + \frac{2.3RT}{nF} \log C_s, \tag{1}$$

where E_o is a constant depending on the electrode system, R is the usual gas constant, T is absolute temperature, F the Faraday, and n the number of electrons involved in either the surface adsorption process on the electrode or the number of charges transferred per ion. The quantity n is usually an integer; however, in instances of certain adsorption processes or mixed reactions the value of n need not be a whole integer. For a one-charge process at 25°C, 2.3RT/nF is approximately 59 millivol and the ion-selective electrode has a response similar to that of a pH electrode, approximately 60 millivolts per tenfold change in concentration. Actually, ion-selective electrodes measure activities rather than concentration; however, in the presence of large, unchanging amounts of indifferent electrolytes the ionic strength of the solution is fixed, the activity coefficient becomes constant, and the potential of the electrode is proportional to the logarithm of the concentration.

Because of the logarithmic relation between potential and concentration, ion-selective electrodes exhibit relative rather than absolute error. It is usually fairly easy to obtain the potential of any given solution to within ±1 mV. For a one-charge process this represents a ±4% relative error. This relative error is the same at 0.1 ppm as at 100 ppm of the selected ion. For a two-charge process the relative error becomes about ±8%. (Because relative rather than absolute error is indicated, more precise results require additional laboratory work.)

Ion-selective electrodes, like pH electrodes, require periodic calibration. This is similar to adjusting zero and 100% on a variety of other instruments. This operation is necessary to compensate for changes in the electrode which change the E_o term. The slope remains constant, but as the electrode ages, random, slow drifts, occur which must be compensated for periodically.

The slow drifts, at least for the solid state electrodes, are usually the result of some slow, irreversible adsorption or chemical process occurring on the surface of the electrode. These processes can almost totally destroy the activity of the electrode. Usually, activity can be restored by etching and reactivation of the electrode or by a mechanical grinding followed by chemical reactivation of the fresh surface. It is important to note that these electrodes are active and do undergo certain side reactions, albeit very slow, and thus under prolonged continuous use may require periodic activation. The time between reactivation should be of the order of several months to a year for most practical electrodes.

Ion-selective electrodes are subject to a number of interferences; therefore, one must know at least qualitatively the composition of the solutions being monitored.

The electrodes can be operated in one of several modes, depending on the composition of the stream to be monitored:

(1) The electrodes are directly immersed in the stream to be measured. This mode of operation is most practical when there is a large excess of indifferent electrolyte such as NaCl in saline waters.

(2) A small side stream is taken from the main process stream, and reagents are added to this sample stream before it contacts the ion-selective electrode. This reagent usually adjusts pH and ionic strength.

(3) A side stream is taken from the main process stream, and a standard addition of the ion of interest is made. Measurements are made before and after additions, and the concentration of the original stream is readily calculated from the difference in potential and the amount added. For instance, for a one-charge transfer process a standard addition which produces an 18 millivolt change indicates that the original concentration is equal to the amount added.

(4) The side stream can be automatically titrated with a reagent to any given end point and the original concentration of the selected ion readily calculated.

These are but a few illustrations of the use of ion-selective electrodes in a continuous, or at least semi-continuous, operation.

The following description is presented to illustrate the use of an ion-selective electrode to measure traces of heavy metals at various points in a particular process. In this example samples were taken to the laboratory only because of lack of time and money to obtain the necessary ancillary equipment and set up the experiment in the operating plant.

Samples were obtained from three different points in the Office of Saline Water's desalting plant in Freeport, Texas. The objective of this experiment was to measure the total copper concentration in the brine as it proceeded through the process. In addition, information about the physical form of the copper was desired. Most of the pipes and heat exchanges in this plant are copper. The results obtained in this experiment are presented in Table I. Sample #1 was raw incoming seawater. Sample #2 was obtained after the addition of H_2SO_4 and the deaerator-decarbonator unit. Sample #3 was the final brine discharged.

TABLE I

Analyses by Cu-Au_2S_3 Electrodes of Brines From OSW Desalting Plant, Freeport, Texas

(Samples Taken 10/2/72)

	Sample #1	Sample #2	Sample #3
pH (as received)	8.0	6.3	7.0
Cu^{+2} (ppm) pH 6.0	N.D.*	0.025	0.63
Cu^{+2} (ppm) pH 2.0	N.D.*	0.45	1.44
Cu^{+2} (ppm) pH 6.0 (AA**)	0.001	0.080	1.02
$SO_4^=$ (ppm)	2360	2550	5700

*N.D. = Not Detectable

**AA = Extraction followed by atomic absorption analyses

A Cu -As_2S_3 (1,6), ion-selective electrode (ISE) was used to monitor the samples for Cu^{+2}. The atomic absorption (AA) results were obtained by extracting the sample at pH 6.0. The $SO_4^=$ analyses were performed by titrating with $BaCl_2$ and using an Fe-1173 electrode (7,8,9) to indicate the end point. The pH of the solutions was adjusted by adding dilute HNO_3.

The results presented in Table I indicate there is very little copper (<1 ppb) of any kind in the incoming raw seawater (Sample #1). As the brine proceeds through the process, it begins to pick up copper in various forms. The results for Sample #2 indicate that about 0.025 ppm Cu^{+2} is present (ISE at pH 6) and about 0.425 ppm is present as either a soluble complex or particulate copper (ISE at pH 2 minus ISE at pH 6). The AA results indicate that at pH 6.0, total soluble copper had increased to 1.02 ppm. The $SO_4^=$ results indicate a reduction in brine volume of 55%. The copper concentration in the brine should increase by 223% if there were no additional pick-up during the distillation portion of the process. These results indicate that there has been additional copper disolution, but no significant increase in copper particulate (0.24 ppm copper particulate). In fact, it appears that some of the particulate copper was dissolved during the heat exchanging portion of the process.

This is but one illustration of how ion-selective electrodes can be used to monitor a process. In this case two reasons existed for monitoring: (1) to limit the amount of copper in the final brine discharge, and (2) to monitor the rate of corrosion of the heat exchangers. It should be noted that the accuracy of these laboratory measurements is much better than the results to be expected from a field operation.

Ion-selective electrodes can also be used in laboratories to replace certain existing methods. Previously, the standard method for determining total copper in these brines was to add excess HF to the sample and determine the total copper concentration spectrophotometrically. The HF was added to complex iron and dissolve a variety of siliceous materials which adsorb copper. The standard procedure was carried out with the replacement of the spectrophotometer by an ion-selective electrode as the copper indicator. When HF was added, the copper concentration increased; however, as the CaF_2 precipitated, the copper began to decrease, indicating significant adsorption or coprecipitation of copper. Thus, an ion-selective electrode can be used to measure a variety of kinetic parameters associated with removal of free ions from solution.

Finally, certain precautions should be taken in using ion-selective electrodes. In general, these precautions are very similar to those required for in-line process monitoring of pH or conductivity. The temperature must be known and compensated; the electrode must be kept clean of foreign matter; single point calibration should be performed frequently; and multipoint recalibration should be accomplished periodically. The frequency with which these operations should be carried out is greatly dependent on the nature of the operation, the rate of change of the electrode, the rate of change of the process, and the desired accuracy.

Ion-selective electrodes can be used to continuously monitor a wide variety of aqueous process streams. However, they are just monitors. The cannot be used to replace the analyst in the laboratory, but can be a significant aid in reducing the number of routine analyses required. They are best used to indicate significant concentration changes (>25%) on a rapid, real-time basis. With precise calibration, they can be used to indicate changes as small as a few percent (<5%). Effective use of these electrodes requires qualitative information about the streams to be monitored. Successful applications of these electrodes have been described previously (3,5).

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ANALYTICAL PROCEDURES FOR TRACE HEAVY METALS IN WATER

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It was pointed out by the writer at this conference that trace heavy metal ions in water can exist in three forms, (1) as particulates, (2) as ions, and (3) as complexed with organic entities. Most of the writer's experience has been with ultrapure water systems which require water with resistances of 10 to 18 megohm-cm and with very low particulate counts. For example, the specifications for water used in oncethrough boilers (super critical pressures) of many modern plants are:

Impurity	Max. Limit (PPB)
Total Dissolved Solids	< 50
Silica	< 10 - 20 (some)
Iron	< 5 - 10 (some)
Copper	< 2
Calcium and Magnesium	0
Oxygen	< 5 - 7 (some)
Resistance	> 10 megohm-cm (at 25° C.)

Particulates

Two approaches are used for particulates.

(1) Membrane filter, and
(2) Particle Counters

Membrane filters are applied (1) in a static or (2) dynamic way. In the static procedure water is passed through a membrane of given porosity and the rate of flow is determined. This gives the rate of particulate deposition which is a measure of the concentration. This method is frequently referred to as the "Silting Index".

In the dynamic method the membrane tape continuously passes at a controlled speed and with a constant flow of water passing through the tape. The color and intensity of the deposits give an indication of the type and concentration of particulates. Both white and black filters are available. Such filters can detect particulate solids in the range of 2 to 4 ppb. The accumulated deposits can be analyzed by various chemical or spectrographic methods.

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As these water purification systems use ion exchangers frequently some of the particulates may be sloughed or broken off from the resin particles. If present, these will also deposit on the membrane filters, and therefore must be distinguished from the metal deposits. The resin particles are insoluble in acid or alkali solutions.

A particle counter can give an indication of the size and concentration of particulates at various points of a system so the source of fouling can be traced.

Total Solid Concentration

To determine the solid concentration in the ppb range, a large volume of water is evaporated with an IR lamp as the heat source in a closed system. The water of a given volume is introduced into a silicon dish at the same rate as the evaporation rate. The dish rests on a balance so the weight of the dish and the dish with the solids can be read without transfer.

Ion exchangers are used for concentrating trace quantities of ions when existing in concentration below the limit of a specific method of analysis. The ion is eluted or the resin can be burned and then treated chemically as required for the specific analysis. Cu, Pb, Zn, Co, Ni, Ag, Sr, etc. have been concentrated from natural waters.

To determine the total ionic (cations) concentration in ppb quantities, the water is passed over a cation exchanger in the H form and the conductivity of the effluent is determined. The acid makes the conductivity more sensitive to cations in the range of a few ppb's. This holds if the anion present forms a strong acid with the released hydrogen ion.

Breakthrough of Multivalent Ions

Low cross linked resins show wide changes in volume depending on the valence of the ion. The higher the valance the lower the volume of the resin. Thus, in a softener when calcium and/or magnesium breakthrough the resin in contact with the effluent begins to shrink and the shrinkage is detected photoelectrically so regeneration of the resin can take place.

If a specific resin of low cross linking were available, the change in volume could be an indication of the breakthrough of a specific multivalent ion.

Miscellaneous uses of Ion Exchangers for analysis which may be used as monitoring techniques.

(1) Ion Exchange papers with which rapid qualitative analysis of trace amounts of metallic ions can be made are available.

(2) Many spot tests (microchemical detection) with ion exchange beads are also available. Nearly colorless ion exchange beads are bound with reagents which on reacting with a given metal ion produce a distinct color or decolization. Microchemical detection tests for the following metal ion tests are available--the reagents, type of exchanger as well as the color are well covered by Iczedy (cf. bibliography)

1. Al
2. Ba
3. Bi
4. Cs
5. Cr
6. CrO_4
7. Co
8. Cu
9. In^{3+}
10. Fe^{3+}
11. Ga
12. Ge
13. Hg^{2+}
14. $MoO_4^=$
15. Ni
16. Se^{4+}
17. Th^{4+}
18. Ti^{4+}
19. Tl^+
20. VO_3^-
21. Zr^{4+}

(3) Systems of Chromatographic separation of many heavy metal ions can be accomplished with ion exchangers. The ion exchange texts, especially the analytical books, given in the bibliography have detailed chapters on these separations and analyses.

Precautions

Several precautions must be mentioned.

(1) Many materials of construction will introduce heavy metal ions.
(2) Glass and plastic containers may adsorb some heavy metal ions.
(3) Minute trace of heavy metal ions are found in some of the purest waters.
(4) Ion exchangers should be well purified before being used for analytical work.
(5) The resins themselves have traces of solubility when the strong acid resin is in the H form and the anion exchanger in the OH form.

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"Traces of Heavy Metals in Water: Removal Processes and Monitoring"

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